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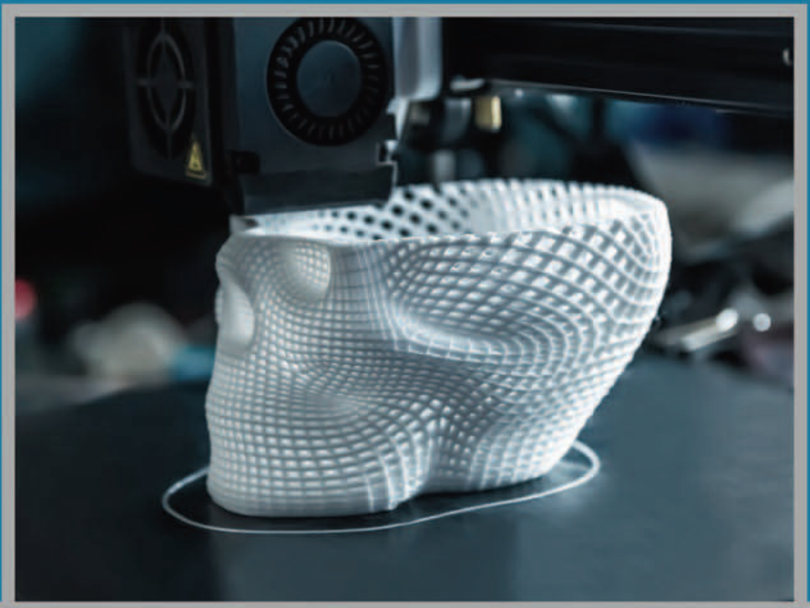

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POLYMERS FOR 3D PRINTING

METHODS, PROPERTIES, AND CHARACTERISTICS

Edited by

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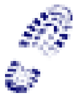
PART I

Introduction to 3D printing



CHAPTER

1

History of the development of additive polymer technologies

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1.1 Introduction to additive manufacturing

Three-dimensional (3D) printing and additive manufacturing (AM) are commonly used terms for additive technologies, where a 3D product is made by adding and combining layers (Fig. 1.1). The terms are often used synonymously; however, it should be emphasized that according to the Standard [1] AM is the official name for the collection of seven main additive processes. Moreover, the term 3D printing is more commonly used for technologies where polymers are the building materials, while AM is more commonly used for those using metals or other materials. In addition, the term 3D printing is commonly used in colloquial language and for low-budget devices. Besides these two terms, other terms have also been used to describe 3D manufacturing technologies, namely rapid prototyping, additive processes, additive techniques, additive layer manufacturing, or solid freeform fabrication [12],

Since 2010, there has been a standard for the terminology of AM, initially ASTM F2792, and now ISO/ASTM 52900:2015, which replaced the previous standard. According to the ISO Standard [1] (ISO/ASTM 52900) AM is defined as "process of joining materials to make parts from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing and formative manufacturing methodologies." The term AM generally refers to a

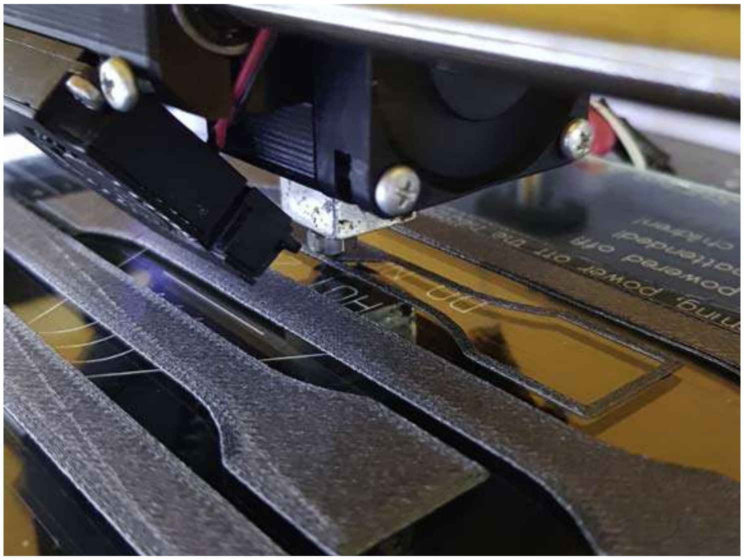

FIGURE 1.1 Example of layer-by-layer printing.

Polymers for 3D Printing
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process and applies to various AM techniques. The process refers to the production of 3D, physical objects built from a computer model, and depending on the purpose and AM technique used, objects can be produced from a variety of materials: polymer, metals and their alloys, ceramics, composites, and even paper, sand, concrete, chocolate, or sugar.

The different AM technologies are briefly classified and described in Chapter 3 followed by a detailed discussion of AM processes used for polymer materials in Chapters 6–12. Various processes differ significantly in terms of the cost of the technology, its quality and accuracy, the time required to complete the process, the finishing processes involved, and the materials used. The range of polymers used is very extensive and has been characterized in detail in Part III of the book in Chapters 13–18 and briefly in Chapter 4.

Initially, AM was a method of rapid prototyping, but with the development of technology and increase in accuracy and quality of objects manufacturing, it found its way into the production of small batch products [3]. Currently, AM is widely used in industry, but is also used by individual users. Among the main application areas are: rapid prototyping, tinkering, personal manufacturing, small batch production, and on demand manufacturing [4]. The application aspects of AM using polymers are discussed in detail in Chapter 5.

1.2 The origins of additive manufacturing

1.2.1 The foundations of modern additive manufacturing

AM is seen as a new and rapidly developing technology, but it is recognized as having been invented nearly 40 years ago (Fig. 1.2). Charles "Chuck" Hull, later founder of 3D Systems [5], is widely recognized as the father of AM process.

However, the origins of this technology can be traced back much earlier. Some [6–9] even refer to the 19th century and point to photosculpture, topography, and weld build-up as the beginnings of 3D printing. For example, in 1860 François Willème created a 3D object using photosculpture methods, while in 1892 Blanther prepared a typographic relief map [8,10].

Stereolithography can also be traced back to a system proposed in 1951 by Munz in which a transparent photopolymer was selectively extruded and cured. In contrast, the first attempt to create objects from photopolymers using a laser took place at Battelle Memorial Institute in the late 1960s. At the same time, the use of a laser beam to cure photosensitive polymers was proposed by Swainson in 1968 [2,8,11].

Other precursors to the development of AM processes included the publication of P. A. Ciraud [12]. In 1972, this Frenchman described a method for producing products of any geometry by adding material in powder form, which laid the foundation for the technology known today as selective laser sintering (SLS). In the same year, Mastubara

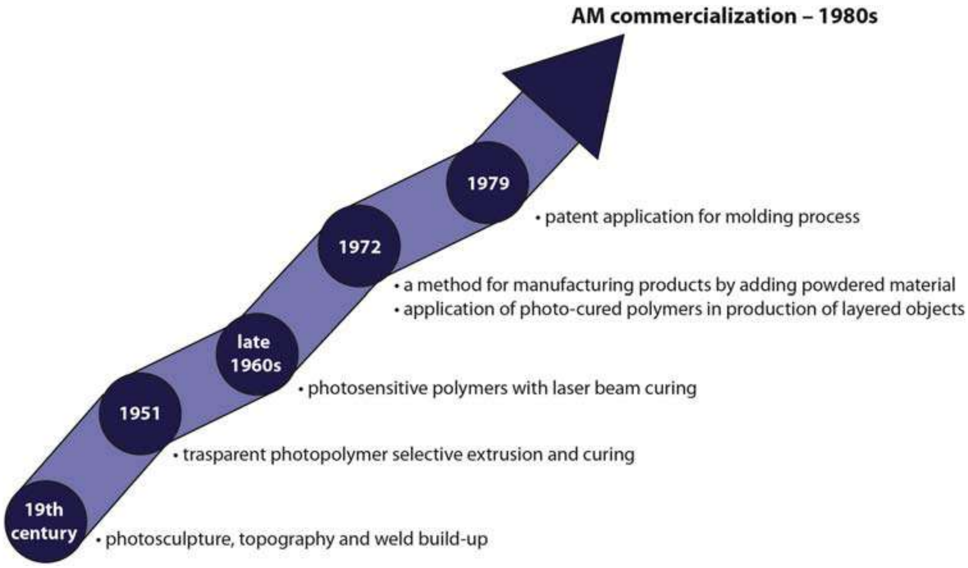

FIGURE 1.2 Foundations of additive manufacturing – milestones.

proposed the use of photo-curable polymers to produce layered objects [10]. In 1979, an American, Ross F. Housholder, filed a patent application [13] for forming 3D ceramic products in the form of layers solidified together. The method was called the molding process and involved selectively solidifying successive layers of sand using heat and a selective mask or controlled heat scanning process. The patent was published in January 1981, but was never commercialized.

1.2.2 The beginnings of additive manufacturing commercialization − 1980s

The 1980s marked the beginning of the commercialization of additive manufacturing (Fig. 1.3). The first commercial rapid prototyping technology is stereolithography. It is considered to have its beginnings in 1980, when Hideo Kodama filed a patent on "Stereoscopic figure drawing device" [14] and in two publications he described the creation of 3D objects from liquid polymer resins [15,16]. Hideo Kodama and Alan Herbert are cited as the first to develop technologies in which a prototype part was actually built, layer by layer, in 1981 and 1982, respectively [4]. In 1984, Alain Le Méhauté, Olivier de Witte, and Jean Claude André were the first to file a patent application for stereolithography. However, the French patent was rejected [17]. In August of the same year, a patent on stereolithography was filed by American Charles W. Hull [18]. This patent was granted in 1986 and related to the first device for production of 3D objects by stereolithography. With legal protection for his solution, Hull founded a company with Raymond Freed called 3D Systems and began producing the first commercial machine working with additive technology. In 1988, these machines were delivered to customers.

In the late 1980s, the Japanese companies NTT Data CMET and Sony/D-MEC also introduced commercial stereolithography devices, which were the Solid Object Ultraviolet Plotter (SOUP) and Solid Creation System (SCS), respectively [16].

In 1989, Scott Crump invented another AM process, fused deposition modeling (FDM), and filed a patent application for it [19]. In the same year, Crump and his wife Lisa Crump founded Stratasys, which commercialized the technology in 1991 by selling the first 3D printer working with FDM technology [4,20].

In 1989, a patent application was also filed for a third AM process, SLS [21]. This had been developed 3 years earlier and gradually refined by Carl Deckard and Joe Beaman at the University of Texas, and then commercialized by their startup DTM Corp, which built SLS machines.

The late 1980s marks not only the beginning of the commercialization of AM, but also rapid development of materials involved. In 1988, the first generation of acrylic resins was introduced to the market, developed together by 3D Systems and Ciba-Geigy. In the same year, Asahi Denka Kogyo launched the first epoxy resin dedicated to the CMET SLS machine produced by NTT Data CMET. At the same time, DuPont Somos also produced a stereolithography machine and materials for it, and Loctite entered the acrylic resin business. In addition, DuPont filed four patent applications in 1989 for the development of photopolymers for stereolithography [16].

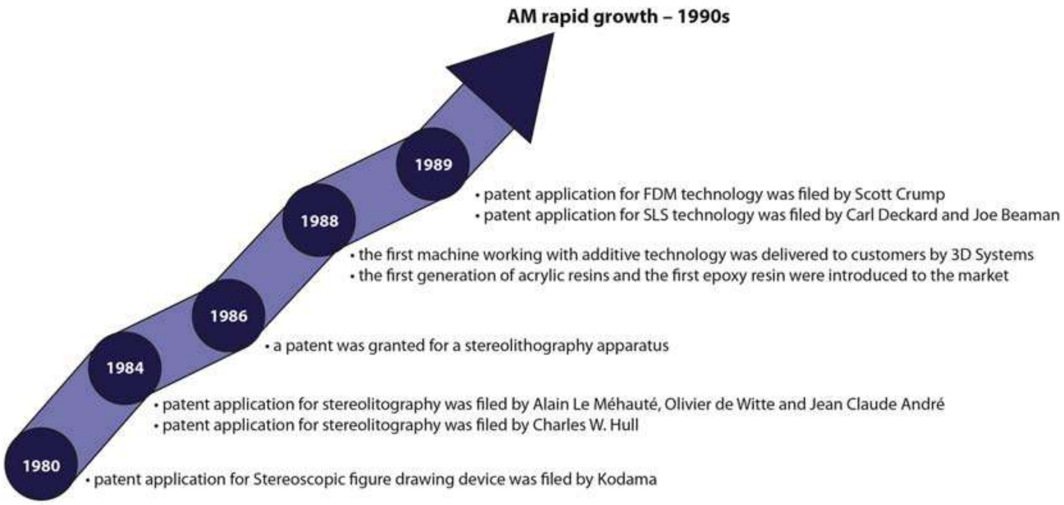

FIGURE 1.3 Additive manufacturing commercialization − milestones.

1.2.3 *Dynamic development of additive manufacturing technologies and emergence of the name 3D printing — 1990s*

The beginning of the 1990s was a time of new patent filings and introduction of new technologies (Fig. 1.4). In 1990 Belgian Materialise was founded — the first company providing 3D printing services in Europe and at the same time one of the first in the world. Simultaneously, the company began to develop its own software for 3D printing to prepare models. In the same year EOS sold its first stereolithographic machine, which today specializes in the production of machines printing from powdered metal (DMLS) and plastic (SLS) [16].

In 1991, besides the previously mentioned FDM technology, two other new technologies were introduced to the market, namely SGC (solid ground curing) by Cubital based on photo-cured polymers and LOM (laminated object manufacturing) by Helisys based on bonding sheets of material. Unfortunately, neither of these two technologies was as successful as FDM and they have already been pushed out of the market [16].

In 1992, DTM introduced SLS and Teijin Seiki produced Soliform stereolithography system. In the same year and the following year, two new resins were introduced to the market; they were vinylether Exactomer resin products for SLA from Allied Signal and epoxy resin products from 3D Systems and Ciba, respectively [10,16].

Another year, 1993, is very important in terms of the introduction of new technologies and the beginning of changes in the AM market. Sanders Prototype, Inc., now Solidscape, unveils a new dot-on-dot technique using wax as the printing material, and the Massachusetts Institute of Technology develops a new AM process based on traditional inkjet printing, now known as Binder Jetting (BJ). Also in this year, another new process based on metals is patented, now called EBM technology, which involves layer-by-layer melting of electrically conductive powder with an electric beam. At the same time, Soligen is commercializing direct shell production casting (DSPC), which involves fusing a ceramic powder with a liquid binder, developed and patented by the Massachusetts Institute of Technology (MIT). Denken, on the other hand, introduces a new SL system using a solid-state laser that is much cheaper and much smaller compared to previously available solutions [22—24].

In 1994, EOS (Electro Optical Systems), which was founded in 1989, sold its first stereo system in which the model is obtained from metal powder selectively melted by laser [11]. On the other hand, in 1995 Fraunhofer Institute developed the selective laser melting process [10].

In 1996, the term 3D printing was coined. At that time, Z Corporation commercialized a technology developed by MIT to create a 3D model by selectively bonding plaster powder with a binder, called 3D Printing (3DP) [22,25]. In 1997, patent "Apparatus for producing parts by selective sintering" [26] was granted. In the same year, AeroMat

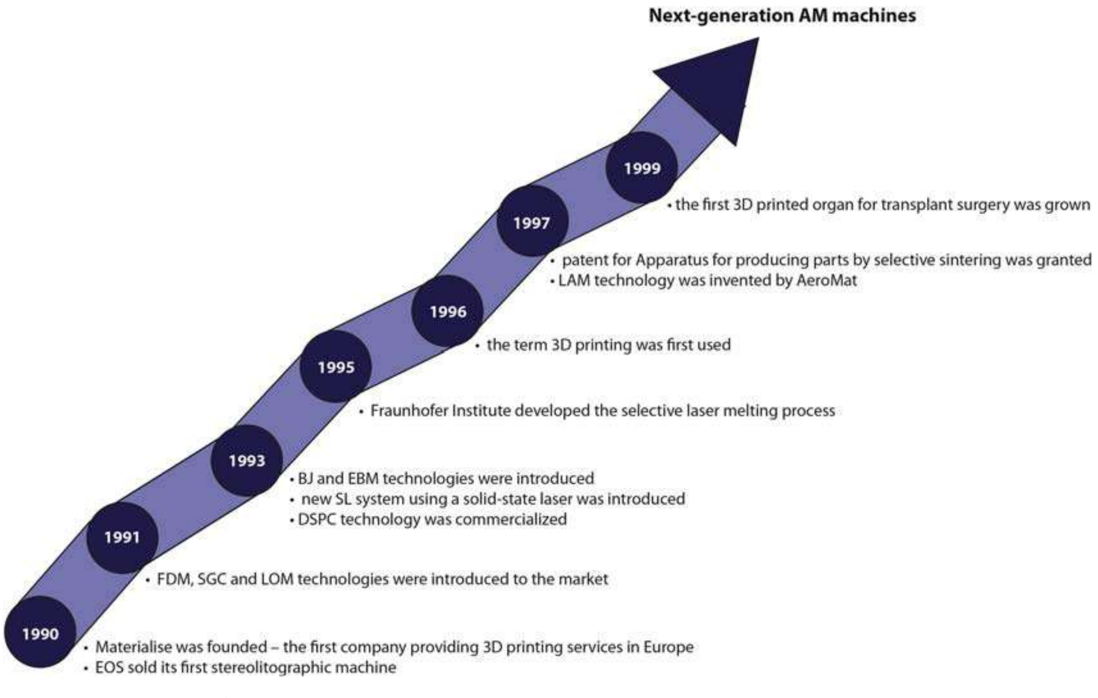

FIGURE 1.4 The rapid growth of additive manufacturing in the 1990s.

invents laser additive manufacturing (LAM) [10]. In 1998, Objet Geometries Ltd. was founded which later introduced PolyJet and PolyJet Matrix methods based on polymer jetting technologies and related materials [27].

The year 1999 was also particularly important in the development of additive manufacturing. It was then that Extrude Hone AM installed its first metal printing machine, the ProMetal RTS-300, at Motorola, while 3D Systems released two very important devices in the additive manufacturing history, namely the SLA 7000 ThermoJet, the most expensive polymer printer of the time, and the ThermoJet, which was very fast and much cheaper than previous models. Moreover, a particularly important development of the late 20th century was "to grow organs from patient's cells and use 3D printed scaffold to support them" [10,22].

1.3 Dynamic development of additive manufacturing and next-generation machines from 2000 to 2010

In the first years of the 21st century, the AM market was dominated by expensive, professional devices that were used in scientific and research facilities or in industrial applications. Further dynamic development of new technologies was observed. In 2000, the first inkjet 3D printer by Object Geometrics and the first multicolor printer by Z Corp. were presented to the market [10,16].

In the following years, the market for major machine manufacturers changed dynamically (Fig. 1.5). Companies changed their names (e.g., Sanders Prototype Inc. changed its name to Solidscape Inc., and Teijin Seiki to CMET Inc.), withdrew from the market (e.g., Helisys, Aaroflex, Cubital), technologies and companies were acquired (e.g., 3D Systems acquired OptoForm, followed by DTM Corp. and RPC Ltd), and new companies were created (e.g., Cubic Technologies). Many new machines were introduced to the market, allowing the use of a wider range of materials, obtaining higher print quality or printing larger objects at the same time at a lower price compared to earlier models of equipment available on the market. There are also many new materials, including new resins from DSM Somos such as a nanocomposite material, a high-elongation material, a low-durometer material, a flame-retardant material, and a resistant to high temperatures material [22].

Another breakthrough year in the history of additive manufacturing was 2005, when Adrien Boyer began work on the RepRap project to create a low-cost, self-replicating 3D printer that prints objects out of plastic [28,28a]. His intention was to create an open access to the technology and expand the group of users to include individual ones as well, rather than its use only in industry, as was the case so far. Indeed, the free availability of the RepRap project influenced the popularization and spread of 3D printing. The RepRap project has not only influenced the popularization of AM using material extrusion process (FFF), but also the market for materials used for 3D printing. Vik Olliver, a member of the project, proposed the use of PLA and made the first PLA filament, which has now become one of the most popular consumables for low-budget, amateur 3D printers. Previously, the material extrusion technology (FDM) used in Stratasys machines primarily used ABS and nylon [28]. In 2008, the first replicated RepRap machines were created and changed expectations for consumer 3D printing [29,30]. In the same year, the website Thingiverse began, where designers could post their files for free download and printing by individual users at home [27]. In the following years, other websites were created where users could share their designs, or sell and buy them, namely: Sketchfab (since 2012), MyMiniFactory (since 2013), Threeding (since 2013), Pinshape (since 2013), Pinshape Inc., 3DLT (2012—2015), Cults 3D (since 2014), and others [31].

The next pivotal moment for 3D printing came in 2009, when its popularity skyrocketed. This was due to the expiration of patents on the technology, access to cheap printers, and government support for the development of advanced additive technologies [32]. It was in 2009 that companies launching low-cost 3D printers began their operations, namely UK-based Bits From Bytes and US-based MakerBot, which further revolutionized the 3D printing industry. After 2009, the AM market changed significantly and material extrusion with FFF and FDM techniques became the dominant process. The use of AM is no longer limited to industrial and scientific applications, but it has become popular in households as well. In the following years, many small companies have emerged to build and sell FFF printers to individual consumers and produce consumables for them.

The offer of companies providing professional 3D printing using various technologies and materials has also expanded significantly. Among the main 3D printing platforms, we can mention iMaterialise (since 1997), which has been operating since the 1990s, or the later emerging Shapeways (since 2007), Sculpteo (since 2009 in Europe), Xometry (since 2013), Jellypipe (since 2017), etc. Another solution is the example of the Aniwa platform, connecting potential buyers with sellers through an online inquiry form [33].

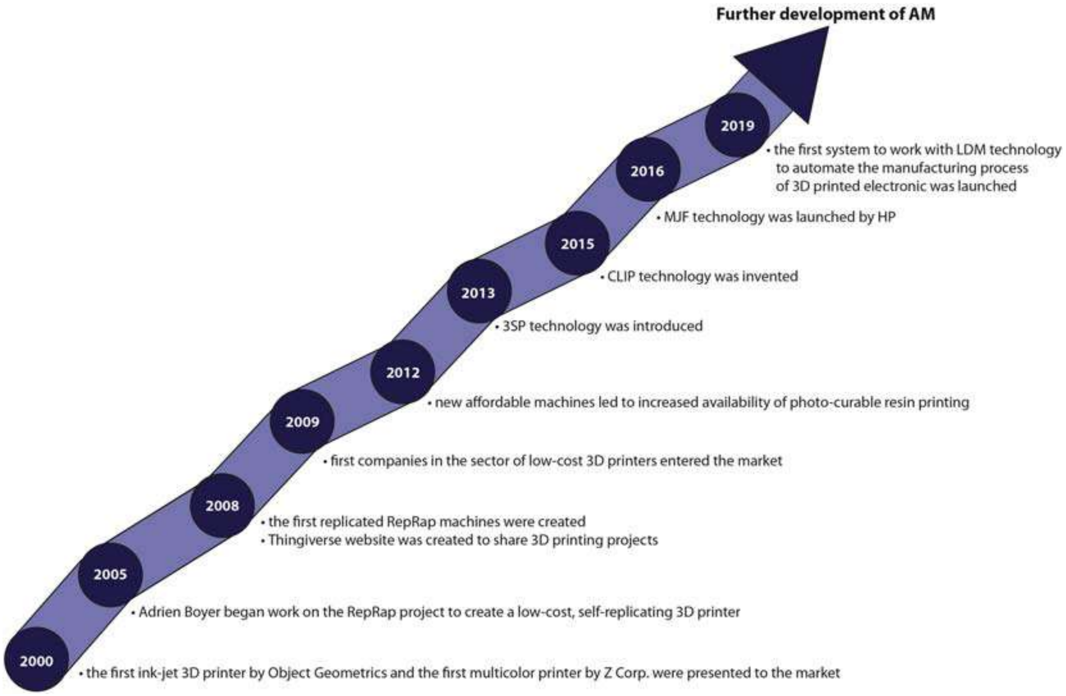

FIGURE 1.5 Additive manufacturing development after 2000 – milestones.

1.4 Contemporary additive manufacturing

Another milestone moment for making additive manufacturing more accessible came in 2012, with developments in photo-curable resin printing. That is when the affordable B9Creator printer using Digital Light Processing (DLP) technology came out, followed a few months later by the Form 1 printer from Formlabs working with Stereolithography technology [27]. Another efficient alternative to SLA printing is 3SP technology introduced in 2013 by EnvisionTEC. In this case, resins are fused with high accuracy using a laser beam.

Further efficiency improvements in the resin 3D printing process were achieved in 2015. That is when DeSimone and colleagues announced the development of a new Continuous Liquid Interface Production (CLIP) technology that is a variation of vat photopolymerization additive manufacturing technology. This method is much faster compared to DLP and SLA processes because the object is produced from the resin in a continuous, layerless manner as a monolithic polymer object [34–36].

In 2016, HP launched its new Multi Jet Fusion (MJF) technology to create high-quality functional parts at higher speeds using Powder Bed Fusion (PBF) process, which also includes SLS mentioned before. MJF uses a polymer powder that is fused layer by layer using infrared light.

Just as important as efficiency is the precision of the printing process, which has been significantly improved with the introduction of the new NanoParticle Jetting (NPJ) technology. It was launched in 2016 as a technology for printing from metal, but has also found application in printing technical ceramics. Printing is done using inkjet print heads to deposit layers of liquid material infused with metal nanoparticles.

That same year, Liquid Deposition Modeling (LDM) technology was developed to deposit a liquid laser-cured composite material (based on acrylic, epoxy, or polyester resins) containing short fibers (e.g., carbon, aramid, glass, basalt, bamboo, cotton, flax). In 2019, the first system to work with LDM technology to automate the manufacturing process (DragonFly LDM) and efficiently 3D print electronic circuits around the clock was launched [37].

Practically since 2010, a continued significant increase in interest in additive manufacturing has been seen, as demonstrated by a steady increase in the number of publications related to AM/3D Printing (Fig. 1.6). Many research centers and universities, as well as research laboratories of major material suppliers for the AM process, are conducting numerous studies on the influence of process parameters on the quality of the products and the implementation of new materials [9]. Among the main research directions are process monitoring, simulation, and new material development.

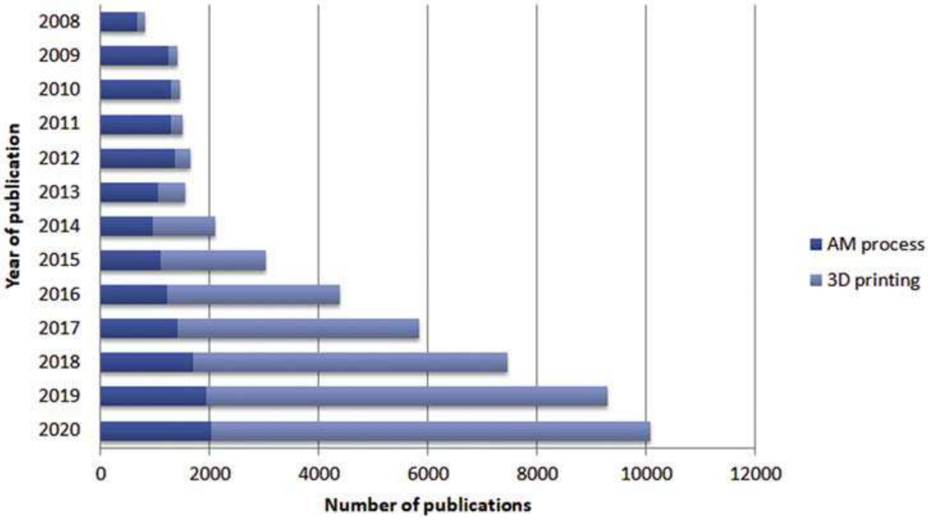

FIGURE 1.6 Number of publications on AM process and 3D printing in respective years (own compilation based on ISI Web of Science).

In recent years, methods have been developed to reduce costs by printing directly from much cheaper polymers in the form of granules or powder, such as powder melt extrusion (PME), fused granular fabrication (FGF), fused particle fabrication (FPF), or pellet additive manufacturing (PAM), rather than purchased, ready-made filaments. Printing directly from polymers in other forms than filament also makes it possible to expand the range of polymers used. In addition, printing speeds using pellets can be much faster than using filament [38].

Recently, the significance of composites in additive manufacturing has also increased. More and more polymer composites are available and used in the market to achieve the expected properties and strength of the printed part with increasingly satisfying printing process performance, lower material costs compared to commonly used metals, and lower energy consumption [39–41]. Further work is also being carried out to increase the use of composites, developing new materials and enabling technologies. Composite materials based on various thermoplastics are filled with carbon, glass, wood, kevlar, or jute fibers, among others [42,43]. In contrast, there is currently a push to develop and build printers that work with FDM technology, where the resin and fibers are combined directly in the extruder [44].

Another current trend in AM is the work on using recycled pellets for 3D printing through extrusion processes [45–48]. Yet another development concept concerns large-format printing, where Robot based 3D printing and large-format 3D printers are used. There is a growing market for such industrial solutions (pellet extruder for robots and CNC machines) as well as new developments in this area [49].

One more materials trend is the use of epoxy resins, enabling fast and low-cost fabrication of complex geometries. Due to their unique properties, they are widely used in such applications as electronics, automobiles, adhesives, and coatings and fiber reinforced composites [50].

Yet another variant of additive manufacturing is 4D printing, which is the printing of intelligent materials that respond in time to external stimuli. Intensive research and development of 4D printing has been going on for several years. In this case, 3D object printed in SLA and FDM technology under the influence of an external factor (e.g., temperature, water, pH, light, etc.) can change its shape, properties, or functionality over time. The dynamic development of 4D technology is closely related to the development of new materials, such as shape memory materials, hydrogels, cellulose composites responsive to humidity, thermoreactive polymers, thermal photoreactive polymers, or such processes like fiber architecture or stress relaxation [51–55].

In 2020, as predicted by Forbs [56], innovations in the AM market were driven by the evolution of AM technologies and their increased efficiency. Undoubtedly, in recent years, it is the efficiency and the limitations of the size of the printed object that are the main constraints to even wider adoption of the technology. Eliminating the need for a chamber in AM machine where certain conditions prevail or a certain environment is produced is another challenge for equipment manufacturers. Finishing process automation as well as software development are also being heavily advanced. This year has also shown new applications for AM processes. Many 3D printers around the world have been used to manufacture personal protective equipment items as well as other ways to combat pandemics. Despite COVID-19 and the apparent slowdown of many sectors around the world, the 3D printing industry continues to grow, although growth in 2021 is slower than in earlier years [57].

1.5 Summary

Over the nearly 40 years of AM development, many technologies have emerged, but not all of them have survived. After the initial rapid advancement in new technologies, the development of the materials applied in them is now of great importance. Particularly significant are polymers, whose availability is very diverse, as well as the variety of their properties and the range of their applications are very wide. The optimal choice of material and parameters of the printing process determine the quality of the finished product; therefore research in this area is particularly important and will enable further market growth.

References

[1] ISO/ASTM 52900:2015 Additive Manufacturing — General Principles — Terminology.

[2] B. Hughes, G. Wilson, Technology and engineering teacher, Reston 75 (4) (Dec 2015/Jan 2016) 18–21.

[3] I. Gibson, D. Rosen, B. Stucker, M. Khorasani, Development of additive manufacturing technology, in: Additive Manufacturing Technologies, Springer, Cham, 2021, pp. 23–51.

[4] E. Matias, B. Rao, 3D printing: on its historical evolution and the implications for business, in: Proceedings of PICMET '15: Management of the Technology Age, 2015, pp. 551–558.

[5] 3D Systems. https://www.3dsystems.com/our-story, 2020 (Accessed March 02, 2020).

[6] D.L. Bourell, J.J. Beaman Jr., M.C. Leu, D.W. Rosen, A brief history of additive manufacturing and the roadmap for additive manufacturing: looking back and looking ahead, US, in: Turkey Workshop on Rapid Technologies, September 24, 2009, pp. 5–11.

[7] D.L. Bourell, Perspectives on additive manufacturing, Annu. Rev. Mater. Res. 46 (2016) 1–18.

[8] Y. Zhai, D.A. Lados, J.L. Lagoy, Additive manufacturing: making imagination the major limitation, J. Occup. Med. 66 (5) (2014) 808–816.

[9] M. Schmidt, M. Merklein, D. Bourell, D. Dimitrov, T. Hausotte, K. Wegener, et al., Laser based additive manufacturing in industry and academia, CIRP Ann. Manuf. Technol. 66 (2017) 561–583.

[10] J.K. Fink, 3D Industrial Printing with Polymers, John Wiley & Sons, Inc. & Scrivener Publishing LLC, Hoboken & Beverly, 2019.

[11] A. Su, S.J. Al'Aref, Chapter 1 – History of 3D printing, in: S.J. Al'Aref, B. Mosadegh, S. Dunham, J.K. Min (Eds.), 3D Printing Applications in Cardiovascular Medicine, Academic Press, Cambridge, MA, 2018, pp. 1–10.

[12] P.A. Ciraud, Process and Device for the Manufacture of Any Objects Desired from Any Meltable Material, FRG Disclosure Publication 2263777, 1972.

[13] R.F. Housholder, Patent US4247508B1, Molding Process, Jan. 27, 1981.

[14] H. Kodama, Patent JPS56144478A, Stereoscopic Figure Drawing Device, 1980.

[15] H. Kodama, Automatic method for fabricating a three-dimensional plastic model with photo-hardening polymer, Rev. Sci. Instrum. 52 (1981) 1770.

[16] T. Wohlers, T. Gornet, Wohlers Report 2016. History of Additive Manufacturing, Wohlers Associates, Inc., 2016.

[17] H.R. Mendoza, Alain Le Méhauté, the Man Who Submitted Patent for SLA 3D Printing Before Chuck Hull, 2015 (Accessed 15.15.2015), https://3dprint.com/65466/reflections-alain-le-mehaute/.

[18] C. Hull, Patent US4575330A, Apparatus for Production of Three-Dimensional Objects by Stereothopography, Mar. 11, 1986.

[19] S.S. Crump, Patent US5121329, Apparatus and Method for Creating Three-Dimensional Objects, Jun. 9, 1992.

[20] Stratasys, 3D Printing & Additive Manufacturing, 2021. https://www.stratasys.com/ (Accessed March 15, 2021).

[21] J.J. Beaman, C.R. Deckard, Patent US4938816A, Selective Laser Sintering with Assisted Powder Handling, Jul. 3, 1990.

[22] T. Wohlers, T. Gornet, Wohlers Report 2014. History of Additive Manufacturing, Wohlers Associates, Inc., 2014.

[23] M. Ziaee, N.B. Crane, Binder jetting: a review of process, materials, and methods, Addit. Manuf. 28 (2019) 781–801.

[24] I. Paoletti, L. Ceccon, The Evolution of 3D Printing in AEC: From Experimental to Consolidated Techniques, 2018. https://www.intechopen.com/books/3d-printing/the-evolution-of-3d-printing-in-aec-from-experimental-to-consolidated-techniques (Accessed November 5, 2018).

[25] P. Ślusarczyk, Historia Druku 3D. (History of 3D Printing), 2017. https://centrumdruku3d.pl/historia-druku-3d/ (Accessed March 9, 2017).

[26] C.R. Deckard, Patent US5597589A, Apparatus for Producing Parts by Selective Sintering, Jan. 28, 1997.

[27] (3dsourced, 2020) 3DSourced, The Complete History of 3D Printing: From 1980 to 2021, 2021. https://www.3dsourced.com/guides/history-of-3d-printing/#1993_-_95_ZCorp_Color_Jet_3D_printing_and_maturation (Accessed March 9, 2021).

[28] M. Petch, Interview: Vik Olliver, the First RepRap Volunteer – 'We Didn't Just Build a 3D Printer', 2018. https://3dprintingindustry.com/news/interview-vik-olliver-first-reprap-volunteer-didnt-just-build-3d-printer-133892/ (Accessed May 29, 2018).

[28a] RepRap, 2020. https://reprap.org/wiki/RepRap (Accessed February 02, 2020).

[29] D. Pechter, History of 3D Printing – Who Invented the 3D Printer?, 2018. https://all3dp.com/2/history-of-3d-printing-who-invented-the-3d-printer/ (Accessed December 23, 2018).

[30] H.-J. Steenhuis, T. Ulusemre, X. Fang, Technology strategy and developments in consumer 3D printers, in: Conference: Workshop "Transitioning 3D Printing from Niche to Mainstream Markets" June 2018, Paris, France, 2018.

[31] Rankred, 40 Best Websites to Download Free STL Files for 3D Printing, 2021. https://www.rankred.com/download-free-stl-files-3d-printing/ (Accessed March 02, 2021).

[32] D. Bourell, J.P. Kruth, M. Leu, G. Levy, D. Rosen, A.M. Beese, et al., Materials for additive manufacturing, CIRP Ann. Manuf. Technol. 66 (2017) 659–681.

[33] L. Sun, G. Hua, T.C.E. Cheng, Y. Wang, How to price 3D-printed products? Pricing strategy for 3D printing platforms, Int. J. Prod. Econ. 226 (2020) 107600.

[34] J.R. Tumbleston, D. Shirvanyants, N. Ermoshkin, R. Januszewicz, A.R. Johnson, D. Kelly, et al., Continuous liquid interface of 3D objects, Science 347 (2015) 1349–1352.

[35] H. He, Y. Yang, Y. Pan, Machine learning for continuous liquid interface production: printing speed modelling, J. Manuf. Syst. 50 (2019) 236—246.

[36] J. Balli, S. Kumpaty, V. Anewenter, Continuous liquid interface production of 3D objects: an unconventional technology and its challenges and opportunities, in: Proceedings of the ASME 2017 International Mechanical Engineering Congress and Exposition. Volume 5: Education and Globalization. Tampa, FL, USA. November 3—9, 2017, https://doi.org/10.1115/IMECE2017-71802.

[37] A. Dror, A New Disruption in Electronics 3D Printing: LDM, Lights-Out Digital Manufacturing, 2019. https://www.3dprintingmedia.network/ldm-lights-out-digital-manufacturing/ (Accessed March 02, 2021).

[38] A.L. Woern, J.M. Pearce, 3-D printable polymer pelletizer chopper for fused granular fabrication-based additive manufacturing, Inventions 3 (78) (2018) 1—17.

[39] A.D. Valino, J.R.C. Dizon, A.H. Espera, Q. Chen, J. Messman, R.C. Advincula, Advances in 3D printing of thermoplastic polymer composites and nanocomposites, Prog. Polym. Sci. 98 (2019) 101162.

[40] M. Chapiro, Current achievements and future outlook for composites in 3D printing, Reinforc. Plast. 60 (6) (2016) 372—375.

[41] J.M. Chacón, M.A. Caminero, P.J. Núñez, E. García-Plaza, I. García-Moreno, J.M. Reverte, Additive manufacturing of continuous fibre reinforced thermoplastic composites using fused deposition modelling: effect of process parameters on mechanical properties, Compos. Sci. Technol. 181 (2019) 107688.

[42] N. Dixit, P.K. Jain, 3D printed carbon fiber reinforced thermoplastic composites: a review, Mater. Today Proc. 43 (2021), https://doi.org/10.1016/j.matpr.2020.12.609.

[43] N. van de Werken, H. Tekinalp, P. Khanbolouki, S. Ozcan, A. Williams, M. Tehrani, Additively manufactured carbon fiber-reinforced composites: state of the art and perspective, Addit. Manuf. 31 (2020) 100962.

[44] S.H.R. Sanei, D. Popescu, 3D-Printed carbon fiber reinforced polymer composites: a systematic review, J. Compos. Sci. 4 (98) (2020) 1—23.

[45] A.L. Woern, D.J. Byard, R.B. Oakley, M.J. Fiedler, S.L. Snabes, J.M. Pearce, Fused particle fabrication 3-D printing: recycled materials' optimization and mechanical properties, Materials 11 (2018) 1413, https://doi.org/10.3390/ma11081413.

[46] S. Chong, G.T. Pan, M. Khalid, T.C.-K. Yang, S.-T. Hung, C.-M. Huang, Physical characterization and pre-assessment of recycled high-density polyethylene as 3D printing material, J. Polym. Environ. 25 (2017) 136—145.

[47] M.A. Kreiger, M.L. Mulder, A.G. Glover, J.M. Pearce, Life cycle analysis of distributed recycling of post-consumer high density polyethylene for 3-D printing filament, J. Clean. Prod. 70 (2014) 90—96.

[48] G.-T. Pan, S. Chong, H.-J. Tsai, W.-H. Lu, T.C.-K. Yang, The effects of iron, silicon, chromium, and aluminum additions on the physical and mechanical properties of recycled 3D printing filaments, Adv. Polym. Technol. 37 (4) (2018) 1176—1184.

[49] Why Using a Pellet Extruder for 3D Printing Has Several Benefits Compared to Traditional Filament Extrusion, 2020. https://robotextruder.com/uncategorized/why-should-you-use-a-pellet-extruder-for-3d-printing/ (Accessed January 21, 2020).

[50] M. Peerzada, S. Abbasi, K.T. Lau, N. Hameed, Additive manufacturing of epoxy resins: materials, methods, and latest trends, Ind. Eng. Chem. Res. 59 (14) (2020) 6375—6390.

[51] X. Kuang, D.J. Roach, J. Wu, C.M. Hamel, Z. Ding, T. Wang, et al., Advances in 4D printing: materials and applications, Adv. Funct. Mater. 29 (2019) 1805290.

[52] J. Lee, H.C. Kim, J.W. Choi, I.H. Lee, A review on 3D printed smart devices for 4D printing, Int. J. Precis. Eng. Manuf. Green Technol. 4 (2017) 373—383.

[53] A. Bagheri, J. Jin, Photopolymerization in 3D printing, ACS Appl. Poly. Mater. 1 (4) (2019) 593—611.

[54] D. Saritha, D. Boyina, A concise review on 4D printing technology, Mater. Today Proc. 46 (2021), https://doi.org/10.1016/j.matpr.2020.12.016.

[55] M. Quanjin, M.R.M. Rejab, M.S. Idris, N.M. Kumar, M.H. Abdullah, G.R. Reddy, Recent 3D and 4D intelligent printing technologies: a comparative review and future perspective, Proc. Comput. Sci. 167 (2020) 1210—1219, https://doi.org/10.1016/j.procs.2020.03.434.

[56] M. Annunziata, 2020: The Year Ahead in 3D (Printing), 2019. https://www.forbes.com/sites/marcoannunziata/2019/12/17/2020-the-year-ahead-in-3d-printing/?sh=5378267e407f (Accessed December 17, 2019).

[57] J. van Rensburg (Ed.), Wohlers Report 2021. Additive Manufacturing and 3D Printing State of the Industry, Wohlers Associates, Inc., 2021.

CHAPTER

2

The concept of 3D printing

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2.1 Concept of additive manufacturing

Thanks to additive manufacturing (AM), it is possible to create both simple projects by beginners or hobbyists, as well as creative and complex projects with specialized uses in such specific applications as medicine, aerospace, or automotive industry. The scale of the print is also very diverse. The smallest printed objects can have dimensions of a few centimeters or even tens of micrometers, while the largest are even several meters long and have a volume of several hundred cubic meters [1,2].

AM, commonly named three-dimensional (3D) printing, is not simply one of many manufacturing methods [3–7]. This term covers seven main processes (see Chapter 3) and many different materials (see Chapter 4), which are selected depending on the type of manufactured spatial object and its applications. Appropriately selected, they allow for the fabrication of prototypes or unique, personalized one-off or short-run spatial products.

In AM, devices using a light source or laser are used to combine powdered materials into thin layers or to solidify successive layers of liquid polymer resins. The polymer can also be extruded layer by layer by melting a filament or pellet. There are also methods using two materials, i.e., the powdered material is bonded layer by layer with a sprayed binder [3,8–10].

The application of individual layers can be done from above by applying a layer on top of a previously fixed layer, which is characteristic of most methods. However, subsequent layers can also be built up below previously fixed layers, as is the case, for example, in DLP technology.

The execution of AM requires the consideration of four key elements: a 3D computer model, software to process the model, a machine or printer that works with any of the 3D technologies, and the material to be used (Fig. 2.1).

A 3D computer model can be acquired by scanning an existing object or designed in computer-aided design (CAD) programs (Fig. 2.2). The computer model needs special preparation for AM, namely planning its proper location on the working platform (see Section 2.4) and dividing it into layers from which the object will be made. This is accomplished using model processing programs, the so-called slicers. Configuration of slicer requires parametrization of all aspects of the print, and may require an extensive experimentation to get the quality right. In certain cases, a significant part of the parameters can be set automatically based on the available profiles for a given printer model. The materials used for AM can be metals, ceramics, plastics, or even other malleable materials like chocolate. As far as the polymers discussed in this publication are concerned, they can be in liquid (photopolymer resins) or solid form (in the form of powders, pellets, wire, filament, film, or sheets) depending on the technology [9,11].

FIGURE 2.1 Flowchart of the model development and AM processes.

Polymers for 3D Printing
https://doi.org/10.1016/B978-0-12-818311-3.00017-3

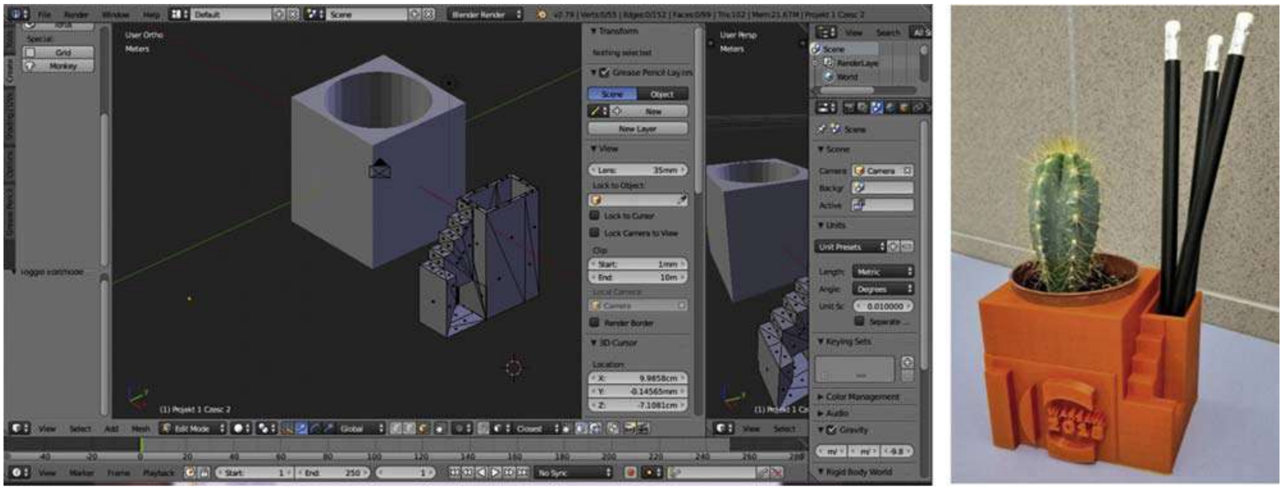


FIGURE 2.2 Model design and completed object printed in FDM technology. *(Reprinted from Ref. [12]).*

2.2 3D modeling

3D models can be created in various ways, namely algorithm-based modeling, manual modeling on a computer, and scanning an existing object. CAD packages or modeling software, 3D scanners or digital cameras, and photogrammetry software are used to prepare them. In order to obtain more realistic and detailed models, it is possible to apply textures (texture mapping) to their surface. There are three types of models: wire-frame 3D models, surface models, and solid 3D models [2,10,11,13,14].

2.2.1 Types of modeling software

Depending on the type of object being designed, different types of modeling programs are available: solid, sculptural, parametric, and mesh. Solid modeling programs (e.g., Autodesk 123D, SketchUp, Tinkercad) are quite intuitive; moreover they allow to set precise dimensions of objects and their cohesion and integrity regardless of the level of complexity. Sculpting programs (e.g., Sculptris, ZBrush), thanks to tools for free shaping of the modeled object (cutting, compression, twisting, stretching), are designed for modeling organic objects such as human faces, but are not suitable for designing precise mechanisms. Parametric modeling programs (e.g., OpenSCAD) work on a different principle than the previously discussed and define the object not by drawing it but by entering commands specifying the components of the object and the way they are connected, which makes it possible to model very precise details. Mesh modeling programs (e.g., Blender, 3Ds Max, Maya, Modo) allow for the creation of complex, precise objects, but are complicated by the fact that the object is created from meshes composed of small triangles where, with little design experience, mesh inconsistency can be an issue [15]. Solid and mesh modeling programs are the most popular (Fig. 2.3), with the former being the most popular choice

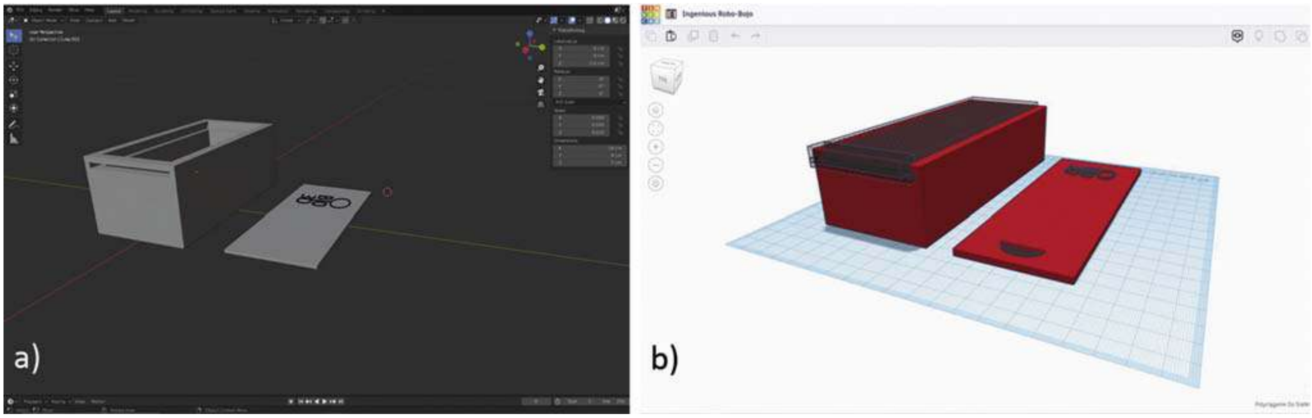


FIGURE 2.3 3D model being prepared in (A) Blender, (B) Tinkercad. *(Reprinted from Ref. [17]).*

for those starting out in 3D modeling. In recent years, with significant advances in AM technologies and capabilities, making modeling in traditional computer-aided design and manufacturing (CAD/CAM) systems faces significant challenges [16].

2.2.2 *File formats for 3D models*

Models prepared for AM must be saved in a suitable format for the process. One of the more popular formats dedicated to all AM technologies is STL (Standard Tessellation Language), developed by Albert Consulting Group for the 3D Systems consortium in 1987 and updated in 2009. The STL file divides the model into triangles; their number and size determines the quality of the produced object—the more smaller triangles the object will be smoother, especially in the case of curved surfaces. However, this can lead to large file sizes and cause performance issues. STL files describe only the geometry of the surface of the 3D object itself without any representation of color, texture, or other typical attributes of a CAD model [5,6]. Another popular file format is OBJ, which unlike STL can retain color and texture profiles or PLY (Polygon File Format), which was originally used to save scanned 3D objects. More than 30 file formats are available for AM. These include the previously mentioned formats such as STL, OBJ, PLY, or AMF (open format developed by the American Society for Testing and Materials (ASTM)), 3MF (created as a dedicated format for 3D printers), 3DS (file format used by Autodesk 3ds Max software), 3DM (open standard used by Rhinoceros 3D software), X3D (eXtensible 3D which is an ISO/IEC royalty-free standard), VRML (Virtual Reality Modeling Language), WRL (format used by VRML), SCL (Stereolithography Contour), SLI (from 3D Systems), CLI (from EOS), HPGL (Hewlett–Packard Graphics Language from Hewlett–Packard), DXF (Data Exchange Format), STEP (Standard for Exchange of Product Data), STP (ASCII text file), MXP (Material Exchange Format), MGX (associated with Micrografx Designer), or IGES (Initial Graphics Exchange Specifications) [18,19].

2.3 Design rules for additive manufacturing

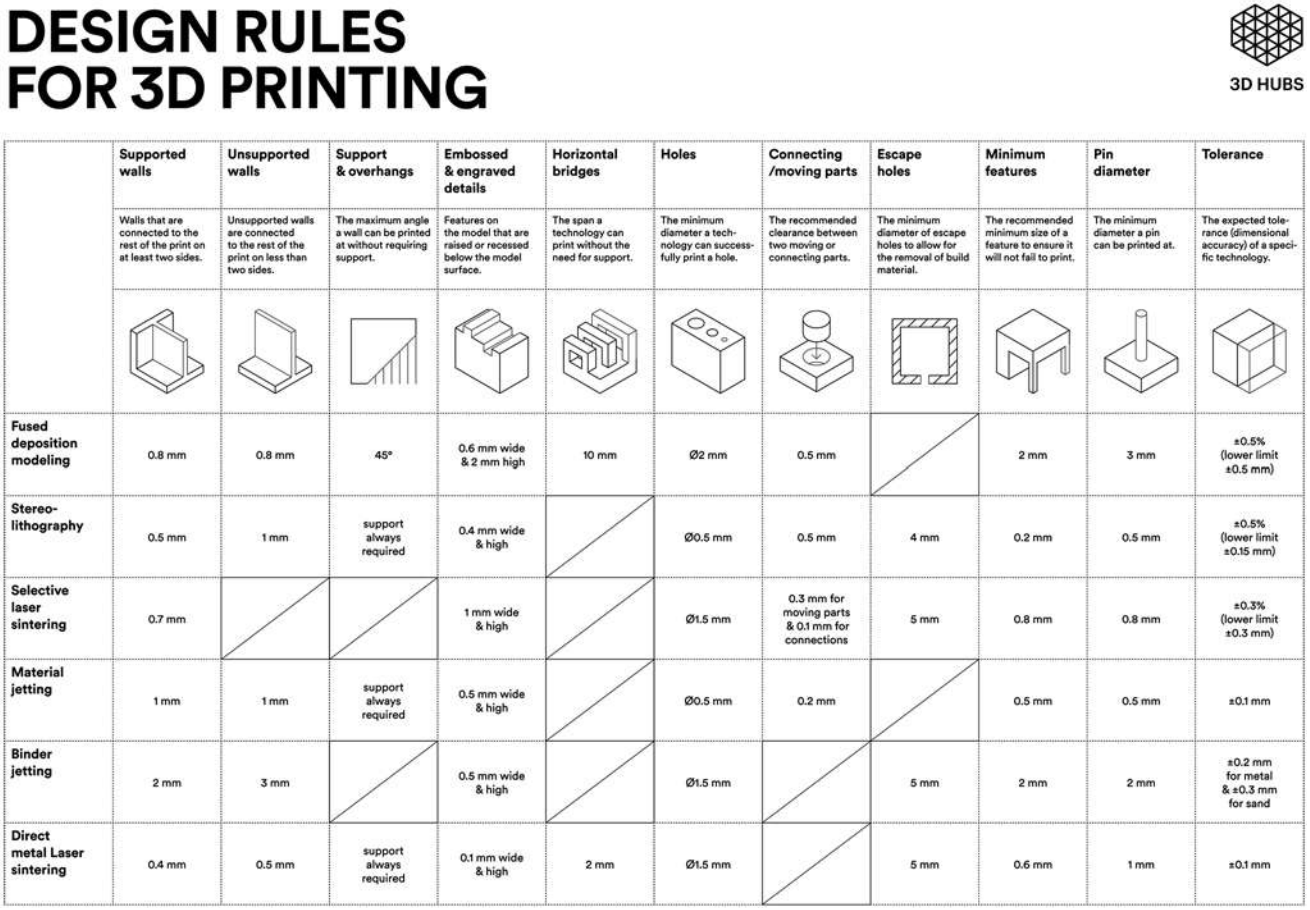
With the popularization of AM, new design methodologies dedicated to additive manufacturing have been developed called Design for Additive Manufacturing (DFAM), which are inspired by Design for Manufacturing and Design for Assembly. DFAM is defined in various ways. One of the definitions describing the issue well is proposed by Laverne et al. [20], where "DFAM is the set of methodology and tools that help the designer to take into account the specificities of additive manufacturing (technological, geometrical, pre/post processing …) during the design stage." There are two types of DFAM: DFAM Concept Assessment and DFAM Decision Making. The former helps designers in selecting AM technologies. DFAM Decision Making, on the other hand, is designed to help the designer find solutions by applying some of the available approaches: DFAM guidelines, DFAM Design Optimization, DFAM Geometrical Validation, and DFAM Product Properties [20].

Design guidelines for specific AM technologies developed with the limitations of those technologies in mind are critical to properly designing a product and selecting the right technology to make it. Designers match their designs to manufacturing processes and must consider the specific technology's constraints [5,10,21–25]. Fig. 2.4 shows the key design principles for six commonly used AM technologies. Sections 2.3.1–2.3.5 describe the limitations of the five chosen most popular and widely used technologies in more detail and identify possible design solutions to achieve high-quality prints.

2.3.1 *Design rules for FDM*

FDM 3D printing, like any AM technology, has some design limitations and occurring problems during printing. The main ones include: bridging, reduced dimensions of holes in the vertical axis, proper execution of overhangs, sharp edges, corners, and well-fitting pins, and complex design that lead to problems during printing [27].

Bridging occurs when the printer must print between two supports or anchor points where an unsupported layer must be suspended in air, which can cause material to sag. The bridging problem usually occurs in holes with a horizontal axis or in the top layer of hollow parts. It can be solved in two ways: by using supports or reducing the bridging distance. The use of supports, however, will entail the need to remove them later and the traces left behind requiring finishing. Eliminating overhangs, on the other hand, would require reducing the size of the bridge below 5 mm, otherwise overhangs will occur and get larger as the distance increases [5,27].



DESIGN RULES
FOR 3D PRINTING

3D HUBS

	Supported walls	Unsupported walls	Support & overhangs	Embossed & engraved details	Horizontal bridges	Holes	Connecting /moving parts	Escape holes	Minimum features	Pin diameter	Tolerance
	Walls that are connected to the rest of the print on at least two sides.	Unsupported walls are connected to the rest of the print on less than two sides.	The maximum angle a wall can be printed at without requiring support.	Features on the model that are raised or recessed below the model surface.	The span a technology can print without the need for support.	The minimum diameter a technology can successfully print a hole.	The recommended clearance between two moving or connecting parts.	The minimum diameter of escape holes to allow for the removal of build material.	The recommended minimum size of a feature to ensure it will not fail to print.	The minimum diameter a pin can be printed at.	The expected tolerance (dimensional accuracy) of a specific technology.
Fused deposition modeling	0.8 mm	0.8 mm	45°	0.6 mm wide & 2 mm high	10 mm	Ø2 mm	0.5 mm	/	2 mm	3 mm	±0.5% (lower limit ±0.5 mm)
Stereo-lithography	0.5 mm	1 mm	support always required	0.4 mm wide & high	/	Ø0.5 mm	0.5 mm	4 mm	0.2 mm	0.5 mm	±0.5% (lower limit ±0.15 mm)
Selective laser sintering	0.7 mm	/	/	1 mm wide & high	/	Ø1.5 mm	0.3 mm for moving parts & 0.1 mm for connections	5 mm	0.8 mm	0.8 mm	±0.3% (lower limit ±0.3 mm)
Material jetting	1 mm	1 mm	support always required	0.5 mm wide & high	/	Ø0.5 mm	0.2 mm	/	0.5 mm	0.5 mm	±0.1 mm
Binder jetting	2 mm	3 mm	/	0.5 mm wide & high	/	Ø1.5 mm	/	5 mm	2 mm	2 mm	±0.2 mm for metal & ±0.3 mm for sand
Direct metal Laser sintering	0.4 mm	0.5 mm	support always required	0.1 mm wide & high	2 mm	Ø1.5 mm	/	5 mm	0.6 mm	1 mm	±0.1 mm

FIGURE 2.4 Design rules for AM processes. *(Courtesy of: HUBS, reprinted from Ref. [26]).*

The reduction in the dimensions of the holes in the vertical axis is caused by the nozzle pressing the freshly extruded layer of material against the earlier ones to achieve satisfactory layer bonding. The compressive force leads to a deformation of the circular shape into an elliptical shape, and the smaller the hole the more significant the problem. Other factors that contribute to this issue are the equipment used to print, the type of material, and the software used to cut the layers. Slicers allow to reduce or eliminate the problem of deformation of the diameter of holes, but in the case of holes demanding high precision it is recommended to design them with a smaller diameter and then reaming them when finishing them [27].

Correct execution of overhangs is related to ensuring proper support by the surface below the extruded layer. Typically, good quality printed overhangs can be achieved with an overhang angle of up to 45°; however, it also depends on the size of the model; and for bigger objects it may be necessary to increase the angle to 55°. It is highly dependent on the type of material, but at this angle the layer is supported by 50% of the previous layer, which should eliminate the problem of the layer bulging down, curling, or poor adhesion. For wall angles above 45°, it is recommended to use a support when printing [5,19,27].

Making sharp edges and corners is limited due to the design of the printer itself and its circular print nozzle. The edges will never be completely rectangular—they will have a radius equal to the size of the nozzle. When printing pins, on the other hand, you may have a problem with them bonding to the previous print layer or not printing them. With large pins over 5 mm in diameter, this problem does not occur as they are printed with a perimeter and fill. The solution with smaller pins is to properly calibrate the printer and add a small fillet at the base of the pin, or possibly omit the pin from the design and replace it with a hole where the finished pin will be added during the finishing processes [27].

Complex structures with many overhangs or bridges are problematic to print and require a large number of supports, thus increasing the printing time, amount of material used, and requiring complex finishing later. An efficient solution is to divide the model into parts and then glue them together (Fig. 2.5). Particularly important with complex designs is how the printed model is placed on the printing platform. Rotating it by 90° can often eliminate some of

FIGURE 2.5 Printing of a telephone stand with a house-shaped support (A) in full, with an apparent problem of dangling threads during printing of the roof and writing on the wall, (B) in two parts, flat, which positively influenced the quality of printing. *(Reprinted from Ref. [28]).*

the problems (Fig. 2.5). In addition, the printing direction, or orientation of the layers, has a significant impact on the strength of the model. Due to the anisotropic nature of printing, it is weaker in one direction. Also, delamination between layers can occur (also referred to as layer separation) as a result of poor layer-to-layer adhesion. The quality and durability of the model is also determined by the continuity of the paths and the tensions present [27].

Models designed for FDM printing should have walls 0.8−1.2 mm thick, respectively, depending on the kind of filament used and the size of the model. When printing with two heads and two materials—one soluble for making supports—it is possible to print interlocking and moving parts. Such simultaneously printed parts should have a minimum clearance of 0.4 mm. If text or small details are placed on the model, better quality will be achieved with engraved text and details than with embossed ones. The recommended sizes for engraved text or details are a minimum line thickness of 0.6−1 mm and a depth of 0.3 mm, and for embossed ones a line thickness of at least 2.0−2.5 mm and a depth of at least 0.5 mm [19,27].

2.3.2 Design rules for SLA

An important design constraint for models printed in SLA technology is the need for proper orientation during printing (see Section 2.4.2) in order to eliminate print defects or even print breaks due to adhesion of the object to the tray. The necessary reduction of the cross-sectional area in the *z*-axis is usually associated with the need to add a significant number of supports to the model, which may adversely affect the aesthetics of the finished product and should be taken into account when constructing the object. The supports have a treelike structure and at the contact points small marks will be visible on the surface with a smooth finish, which require postprocessing [5,29].

Models intended for SLA printing should have elements with a minimum size of 0.2 mm and walls of 0.4 and 0.6 mm, respectively, depending on whether they are supported or unsupported. Unsupported walls (connected to the rest of the print on less than two sides) using smaller values may warp or detach from the print. To eliminate the problem of walls pulling away, a rounded base should also be used where they connect to the print. For angled walls, it is recommended to use a print support to eliminate warping. The same applies to overhangs of any kind, but they may be unsupported if their length is less than 1.0 mm and the angle of inclination from the horizontal is at least 19°. For bridges, the limitation to printing them successfully is their length—for wider bridges, the recommended length should not exceed 21 mm, thinner ones can be a little longer [29,30].

SLA printing allows for obtaining printouts of high quality and detail; therefore printed objects can successfully include embossed or engraved texts or other details. The minimum height of protruding elements is 0.1 mm above the print surface for embossed elements and the minimum width and thickness of recessed elements is 0.4 mm for engraved elements. The minimum diameter of holes is 0.5 mm regardless of their orientation. Smaller ones may become closed during printing [29].

2.3.3 Design rules for SLS

SLS technology has few design limitations compared to other AM technologies. One of them is avoiding large flat surfaces that can warp. If these cannot be eliminated, then it is recommended to add ribs in the design to support this surface. Any sharp edges will also be rounded off in the printed object. Another issue which needs to be taken into account at the end of the design is the shrinkage of the material caused by the high temperature during printing and the need to increase the dimensions of the entire model before printing. The dimensional increase is done at the model conversion stage before printing and is usually at the 3%—3.5% level. Due to the material used to make the models, there may be slight differences in quality between successively printed objects due to slight dimensional deviations and surface texture. Surface directly after printing is satin-matt and slightly rough—grainy to the touch. Finishing processes are required to achieve a glossy, smooth finish [5,31—33].

Models intended for SLS printing should have a minimum feature size of 0.75 mm. However, it is possible to print even elements of 0.5 mm in size. The minimum wall thickness possible to achieve is also 0.3—0.5 mm, although it depends on the type of material and laser used. For PA12 powder, a thickness of at least 0.7—1.0 mm is recommended, while for carbon-filled PA the minimum is 2.0 mm. A wall thickness of at least 1.0—1.3 mm is considered to guarantee repeatable results. The diameter of the designed holes must not be less than 1.5 mm. Smaller ones may become plugged by uncooked sand and require opening mechanically [31—34].

The advantage of SLS technology is the ability to print moving, matching parts in a single cycle. It requires designing clearances between moving, functional parts of assemblies of at least 0.3—0.6 mm to ensure removal of excess powder. It is also possible to design and print hinges, for which the minimum recommended thickness and length are 0.3—0.8 and 5 mm, respectively. The dimensional accuracy for the powder sintering process depends on the printer, the size of the printed part, and the powder used. However, the accuracy is high—up to ±0.3% of the part dimensions (min. 0.3 mm). Engraved or embossed details or texts require much higher depths or heights than SLA technology due to accuracy and finishing (media tumbling), but can be successfully placed on models. The recommended minimum depth and height of details is 1 mm, while the height of text is about 2 mm, i.e., type grade 14 pt. In addition, texts should be in a sans serif font, and for more fragile letters, a sketch should be added to the text [32—34].

In order to reduce component weight and powder consumption, it is also possible to print hollow models. This requires designing an exit hole with a minimum diameter of 3.5 mm to remove uncooked powder from the center of the object [31,33].

2.3.4 Design rules for Material Jetting

The MJ method produces multicolor, multimaterial prints with a high degree of accuracy as well as design complexity. Its advantage is a smooth, homogeneous surface, but the design limitation is the fragility of the produced objects. Models can be produced in either a matte or glossy setting. The matte setting involves adding a thin layer of support material over the entire outer surface of the print, while the glossy setting uses support material only where technologically necessary to properly print the model [35].

Multicolor models require color space information (CMYK) at the design stage and any textures to be included in the CAD file (exported as VRML) or RGB color to be assigned to object parts during the print setup process.

Multimaterial models can use two materials in the same tray when printing, or even if the device allows it, combine them to create a material with new properties. When designing with two materials, assemblies should be built in native CAD so that different parts can be assigned to different materials during preprocessing. It is important to ensure that there is no body overlap and that die clearance is "0" [35].

Models intended for MJ printing should have elements with minimum dimensions of 0.25 mm. It is recommended that walls be at least 0.5 mm thick, unless they are major load-bearing walls, for which an increase in thickness to at least 1.0 mm is recommended. The diameters of holes and pins should not be less than 0.5 mm and the orientation of holes should be vertical to eliminate problems with roundness. Also, the minimum depth and height of engraved and stamped components, respectively, should be at least 0.5 mm. Any kind of overhangs, bridges, sloping walls, protrusions, and recesses require the use of supports that are printed in the same process as the model, but with soluble material easy to remove in postprocessing. The support material will also be incorporated into the gaps between moving assembled parts, hinges, or joints, for which clearances of 0.15–0.4 mm must be designed around all sides [30,35].

2.3.5 *Design rules for Binder Jetting*

The BJ method, like the MJ method, makes it possible to produce multicolored prints. For this to be possible, the files containing the design must contain color information, which can be added in two ways, as a texture map or on a per face basis. The first way allows for better effects and more detail.

When designing models dedicated for printing in BJ technology, despite the fact that there are no errors associated with thermal effects (characteristic, for example, for FDM, or SLS), it is necessary to remember about the occurrence of significant shrinkage of the material during sintering processes or a little smaller shrinkage at infiltration. The amount of shrinkage also depends on the geometry of the model and its size. Therefore, the object must be scaled appropriately before printing [36].

The method of print curing not only affects shrinkage, but when choosing infiltration also affects the design and the need to add stilts to allow infiltration of the bronze into the part. Stilts need to be placed on a smooth surface with a minimum area of 1.5 × 1 mm, and are removed after infiltration. However, they can affect the appearance of the surface on which they were placed [37].

Thin parts are also a design limitation, as they are very fragile immediately after printing and can be damaged when the object is removed from the powder in the printing machine and consequently transported. Only further processing steps to fix the model (infiltration or sintering) prepare it for use, which is important to keep in mind. Therefore, it is recommended that the minimum wall thickness as well as the size of the minimum component be at least 2.0 mm. Unsupported walls such as ribs or louvers should be at least 3.0 mm and unsupported edges should be 2.0 mm, but with length limited to 20 mm. The minimum diameter of holes should not be less than 1.5 mm and the depth or height of stamped or engraved details should be at least 0.5 mm. Because of the risk of damaging the edges of the model before postprocessing they should not be sharp but rounded and the recommended radius is min. 1.0 mm [37].

If the designed object requires more delicate parts with dimensions smaller than recommended, it is possible to add reinforcing structures that are removed after the curing treatment to strengthen the object to allow it to be removed from the machine and processed. However, such a solution is time- and cost-intensive [37].

2.4 Preparing a file for printing

Regardless of the AM technology used, a number of process parameters that determine the quality of the print and the process flow must be set before the AM process can begin. Specialized software dedicated to specific technologies and devices is available, which allows not only to divide the model into layers, but also to determine the parameters of the AM process. In addition, the advanced ones will check the correctness of the model file. For example, in the Binder Jetting technology, specialized software converts the 3D model into a bitmap, which precisely defines the places on which the head sprays liquid binder. In FDM/FFF technologies, dedicated software divides the model into layers of appropriate thickness—defined by the user and the printer's capabilities.

Typically, the AM system software has a visualization tool that allows the user to view and manipulate the model. The software may also allow the user to change the orientation or location of the design in the printing machine, to scale the design or duplicate it, or even to arrange several parts from different files in the machine [14]. The preliminary setup of the printing parameters using the AM system software is very useful; some of the parameters can be entered automatically, thanks to the previously prepared profiles for the device and material, thus reducing the time of preparing the machine for printing and eliminating possible errors.

2.4.1 Slicing process

A model saved in an AM format such as STL requires appropriate preparation before being sent to a 3D printer and printed. The 3D coherent design must be turned into a specific sequence of commands that will allow the 3D printer to print the object. In FDM technology, this will include moving the print head along a specific path, while keeping in mind the amount of filament extruded by the head, depending on the thickness of the cut layer. Cutting into layers is implemented by programs called slicers [2,6,38—40]. As in the case of 3D modeling software, there are many software products available on the market dedicated to different technologies, containing appropriate functions for preparing the file for AM.

Examples of slicer software used in FDM/FFF technology for preparing print file are, e.g., Ultimaker Cura, Slic3r, KISSlicer, Simplify3D, Tinkerine Suite, Prusa Slicer, SelfCAD, Netfabb, Repetrier-Host, or OctoPrint. The generated file has GCODE extension and contains information such as head and table position, movement speed, or head and table temperature.

When printing complex objects, it is often necessary to use supports for some elements of the structure. They are not used in powder technologies such as SLS or BJ because there the object is supported by surrounding powder. However, in technologies such as FDM, FFF, or SLA supports are generated automatically by the slicer software. After removing the finished model from the machine it is necessary to remove the supports.

2.4.2 Orientation of models during printing

Depending on the AM technology, different positioning of models on the work table is recommended. It affects the quality of the print, strength properties of the printed object, and the printing process flow.

In case of FDM technology, models are normally positioned at an angle of 90° to the table. Exceptions can be models that require supports or have a nonstandard geometry. When using Vat photopolymerization technology with light-cured resins, models are traditionally placed at an angle of about 45°. Such placement allows for free flow of the resin in which the models are immersed. In addition, it makes it possible to reduce the problem of the print sticking to the photopolymer reservoir, resulting from forces that increase with cross-sectional area in the *Z*-axis of the print. The orientation of SLS-printed powder models can have a positive effect on reducing warping of large, flat model surfaces [31]. In MJ technology, due to the use of soluble material supports in the printed model, the orientation of the model is much more flexible unlike for other technologies [35]. In the Binder Jetting technology, due to the application of vertical powder layers on the table to which the bonding agent is applied and to optimize the use of working space, the models are oriented at 90°.

The orientation of the models during printing can affect the anisotropy and thus the properties of the prints, both mechanical (maximum stress, elongation, and Young's modulus) and thermal (glass transition temperature, heat deflection temperature, and thermal conductivity) [41]. Prints made with FDM technology are highly anisotropic—they have different properties depending on whether the object is printed parallel or perpendicular to the table. The strength of parts in the *Z*-axis (direction of overlapping layers) is lower than in the *XY*-plane [42,43]. In SLS and BJ technologies, anisotropy in the material properties results in weakening of the part in the Z—vertical direction. Yet, depending on the material and process parameters, models created by SLS technology can be nearly isotropic [44,45]. In contrast, SLA prints are isotropic, having nearly identical physical properties in the *X*, *Y*, and *Z* directions, regardless of orientation [46]. The orientation during printing also does not have a significant effect on the properties of models made with MJ technology.

2.5 Summary

The preparation of models for AM and the AM process itself is based on a sequence of similar steps regardless of the AM technology used. These are: concept development, preparation of a digital model for AM and its appropriate preparation for use on the AM machine, file transfer to the machine, setup of the machine, print execution, removal of the object from the machine and its cleaning, optional print finishing, or postprocessing.

Of course, the chosen technology, type of material used, or complexity of the project will influence the design limitations and choice of technology because what is possible to implement in one technology while maintaining satisfactory quality may be completely cost-prohibitive or even technologically impossible in another. It is important to select AM technologies and materials at the conceptual stage, even before starting the modeling, to consider all the design limitations resulting from the type of selected technology and the type of selected material. For proper technology selection, on the other hand, it is crucial to determine whether the project will be used only for prototyping or building the final product and at what production scale, as well as what are the quality expectations and cost constraints.

AM now is available to everyone, both professionals and hobbyists, and anyone can create and print their designs. The AM devices are very diverse (they vary greatly in terms of the cost of their purchase and operation, as well as in terms of ease of use), as well as the software available to create models is available in great numbers (there are numerous free tools available, easy to use, and professional, paid software, giving more possibilities, but requiring more experience and knowledge). With the current advancement of technology and its availability, the range of materials available with varying properties, almost any concept can be realized using AM technology, and over time, with technology advancing so rapidly, it may be that only human imagination would be the limit.

References

[1] S. Goehrke, Some of the World's Largest and Smallest 3D Prints, 2020. https://www.fabbaloo.com/blog/2020/7/29/some-of-the-worlds-largest-and-smallest-3d-prints (Accessed 29 July 2020).

[2] W. Gao, Y. Zhang, D. Ramanujan, K. Ramani, Y. Chen, C.B. Williams, et al., The status, challenges, and future of additive manufacturing in engineering, Comput. Aided Des. 69 (2015) 65−89.

[3] ISO/ASTM 52900:2015 Additive Manufacturing — General Principles — Terminology.

[4] The International Academy for Production Engineering, in: CIRP Encyclopedia of Production Engineering, CIRP, 2014, https://doi.org/10.1007/978-3-642-20617-7.

[5] S. Killi (Ed.), Additive Manufacturing: Design, Methods, and Processes, Pan Stanford Publishing, Singapore, 2017.

[6] B. Dermeik, N. Travitzky, Laminated object manufacturing of ceramic-based materials, Adv. Eng. Mater. 22 (2020) 9, https://doi.org/10.1002/adem.202000256.

[7] M.D. Monzón, Z. Ortega, A. Martínez, F. Ortega, Standardization in additive manufacturing: activities carried out by international organizations and projects, Int. J. Adv. Manuf. Technol. 76 (2015) 1111−1121.

[8] M. Pagac, J. Hajnys, Q.-P. Ma, L. Jancar, J. Jansa, P. Stefek, et al., A review of vat photopolymerization technology: materials, applications, challenges, and future trends of 3D printing, Polymers 13 (4) (2021) 598, https://doi.org/10.3390/polym13040598.

[9] W. Xu, S. Jambhulkar, Y. Zhu, D. Ravichandran, M. Kakarla, B. Vernon, et al., 3D printing for polymer/particle-based processing: a review, Compos. B Eng. 223 (2021) 109102, https://doi.org/10.1016/j.compositesb.2021.109102.

[10] B. Redwood, F. Schöffer, B. Garret, The 3D Printing Handbook: Technologies, Design and Applications, 3D Hubs, 2017.

[11] Y. Zhai, D.A. Lados, J.L. Lagoy, Additive manufacturing: making imagination the major limitation, J. Occup. Med. 66 (5) (2014) 808−816, https://doi.org/10.1007/s11837-014-0886-2.

[12] P. Musiał, Design and Printing of a 3D Prototype of an Advertising Product, Engineering Thesis, Warsaw University of Technology, 2019.

[13] D. Scott-Leslie, 3D Modeling: An Overview of History & Industry Applications, 2019. https://www.cadcrowd.com/blog/3d-modeling-overview-history-industry-applications/ (Accessed 4 May 2019).

[14] I. Gibson, D. Rosen, B. Stucker, Additive Manufacturing Technologies, Springer Science+Business Media, New York, NY, 2015.

[15] A.K. France (Ed.), Make: 3D Printing: The Essential Guide to 3D Printers, Maker Media Inc., 2014.

[16] Y. Song, Z. Yang, Y. Liu, J. Deng, Function representation based slicer for 3D printing, Comput. Aided Geomet. Des. 62 (2018) 276−293.

[17] W. Sikorska, Design and 3D Printing of Eyeglass Cases Using Eco-Friendly Filaments, Master Thesis, Warsaw University of Technology, 2021.

[18] K.V. Wong, A. Hernandez, A review of additive manufacturing, ISRN Mech. Eng. 2012 (2012) 10, https://doi.org/10.5402/2012/208760.

[19] Materialise, Design Guidelines, 2021. https://www.materialise.com/en/academy-manufacturing/resources/design-guidelines (Accessed 12 April 2021).

[20] F. Laverne, F. Segonds, N. Anwer, M. Le Coq, DFAM in the Design Process: A proposal of Classification to Foster Early Design Stages, Conference, Croastie, Sibenik, 2014.

[21] D. Thomas, The Development of Design Rules for Selective Laser Melting, PhD Thesis, University of Wales, 2009.

[22] J. Go, A.J. Hart, A framework for teaching the fundamentals of additive manufacturing and enabling rapid innovation, Addit. Manuf. 10 (2016) 76−87.

[23] M. Mani, P. Witherell, J. Jee, Design Rules for Additive Manufacturing: A Categorization, 2021. https://tsapps.nist.gov/publication/get_pdf.cfm?pub_id=921515 (Accessed 10 May 2021).

[24] M. Leary, Design for Additive Manufacturing, Elsevier, Amsterdam, Oxford, Cambridge, 2020.

[25] ISO/ASTM 52910:2018 Additive Manufacturing — Design — Requirements, Guidelines and Recommendations.

[26] HUBS, Design Rules for 3D Printing Poster, 2021. https://www.hubs.com/get/3d-printing-design-rules/ (Accessed 09 April 2021).

[27] B. Hudson, HUBS, How to Design Parts for FDM 3D Printing, 2021. https://www.3dhubs.com/knowledge-base/how-design-parts-fdm-3d-printing/#:∼:text=%20How%20to%20design%20parts%20for%20FDM%203D,holes%20undersized.%20%20...%20As%20the...%20More%20 (Accessed 09 April 2021).

[28] M. Niedźwiecka, Analysis of the Possibility of Using 3D Printing for the Production of Advertising Gadgets, Master Thesis, Warsaw University of Technology, 2021.

[29] C. Armstrong, HUBS, How to Design Parts for SLA 3D Printing, 2021. https://www.hubs.com/knowledge-base/how-design-parts-sla-3d-printing/ (Accessed 09 April 2021).

[30] 3D Hubs, Core77. Design Rules for 3D Printing, 2018. https://www.core77.com/posts/74401/Design-Rules-for-3D-Printing (Accessed 09 March 2018).

[31] S. Oceanz, HUBS, How to Design Parts for SLS 3D Printing, 2021. https://www.hubs.com/knowledge-base/how-design-parts-sls-3d-printing/ (Accessed 09 April 2021).

[32] Materialise, Design Guidelines for Stereolithography (SLA), 2021. https://www.materialise.com/en/manufacturing/materials/poly1500/design-guidelines (Accessed 09 April 2021).

[33] Xometry Europe, Design Tips for SLS 3D Printing, 2021. https://xometry.eu/en/design-tips-for-sls-3d-printing/ (Accessed 31 March 2020).

[34] proto3000, Selective Laser Sintering (SLS) 3D Printing Design Guidelines, 2021. https://proto3000.com/service/3d-printing-services/materials/overview/design-guidelines/sls-design-guidelines/ (Accessed 09 April 2021).

[35] L. Vassos, HUBS, How to Design Parts for Material Jetting 3D Printing, 2021. https://www.hubs.com/knowledge-base/how-design-parts-material-jetting-3d-printing/ (Accessed 09 April 2021).

[36] P. Dubert, Centrumdruku3D. Jak Działa Druk 3D w Technologii Binder Jetting? (How the Binder Jetting 3D Printing works?), 2021. https://centrumdruku3d.pl/jak-dziala-druk-3d-w-technologii-binder-jetting/ (Accessed 18 November 2020).

[37] A.B. Varotsis, HUBS, Introduction to Binder Jetting 3D Printing, 2021. https://www.3dhubs.com/knowledge-base/how-design-parts-binder-jetting-3d-printing/ (Accessed 09 April 2021).

[38] S. Lefebvre, ICESL: a GPU accelerated CSG modeler and slicer, in: Proceedings of AEFA'13, 18th European Forum on Additive Manufacturing Paris, France, 25−27 June 2013.

[39] M. Šljivic, A. Pavlovic, M. Kraišnik, J. Ilić, Comparing the accuracy of 3D slicer software in printed enduse parts, IOP Conf. Ser. Mater. Sci. Eng. 659 (2019) 012082, https://doi.org/10.1088/1757-899X/659/1/012082. IOP Publishing.

[40] F. Marbun, R.A.M. Napitupulu, C.S.P. Manurung, S. Simanjuntak, Y.-C. Kao, Slicing methodology of A CAD file for 3D printing, IOP conference series: materials science and engineering, volume 852, the 2nd tarumanagara international conference on the applications of technology and engineering (TICATE) 2019 21−22 November 2019, Jakarta, Indonesia, IOP Conf. Ser. Mater. Sci. Eng. 852 (2020) 012074.

[41] C. Greer, A. Nycz, M. Noakes, B. Richardson, B. Post, T. Kurfess, et al., Introduction to the design rules for metal big area additive manufacturing, Addit. Manuf. 27 (2019) 159−166.

[42] S. Gradinaru, D. Tabaras, D. Gheorghe, D. Gheorghita, R. Zamfir, M. Vasilescu, et al., Analysis of the anisotropy for 3D printed PLA parts usable in medicine, U.P.B. Sci. Bull. Ser. B 81 (4) (2019) 313−323.

[43] L. Safai, J.S. Cuellar, G. Smit, A.A. Zadpoor, A review of the fatigue behavior of 3D printed polymers, Addit. Manuf. 28 (2019) 87−97.

[44] J.-W. Oh, S. Nahm, B. Kim, H. Choi, Anisotropy in green body bending strength due to additive direction in the binder-Jetting additive manufacturing process, Korean J. Met. Mater. 57 (4) (2019) 227−235.

[45] M. Monzón, Z. Ortega, A. Hernández, R. Paz, F. Ortega, Anisotropy of photopolymer parts made by digital light processing, Materials 10 (64) (2017) 1−15.

[46] F.T. Senguen, C. Wang, Validating Isotropy in SLA Additive Manufacturing, 2018. https://uvebtech.com/articles/2018/validating-isotropy-in-sla-additive-manufacturing/ (Accessed 21 May 2018).

C H A P T E R

3

Classification of 3D printing methods

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3.1 Classification of additive manufacturing processes

According to the ISO/ASTM 52900 standard [1], there are seven categories of additive manufacturing (AM) processes (Fig. 3.1). These are namely:

- binder jetting (BJT),
- directed energy deposition (DED),
- material extrusion (MEX),
- material jetting (MJT),
- powder bed fusion (PBF),
- sheet lamination (SHL),
- vat photopolymerization (VPP).

Each of the seven main process categories contains different technologies that are still being developed and improved (see Chapter 1). These are briefly discussed in Sections 3.2.1—3.2.7 and in detail in Chapters 6—13 of the book.

In addition to the presented classification of AM processes into seven main groups, they can be classified according to how the layers are applied and then fused and solidified (Fig. 3.2), and by the type of material used (Fig. 3.3) [2—10].

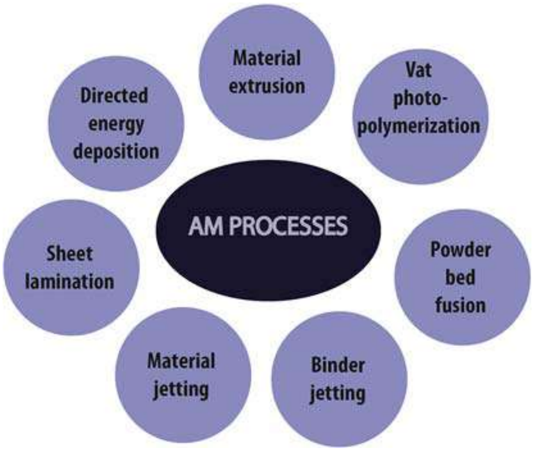

FIGURE 3.1 Classification of additive manufacturing processes according to ISO/ASTM 52900 categories.

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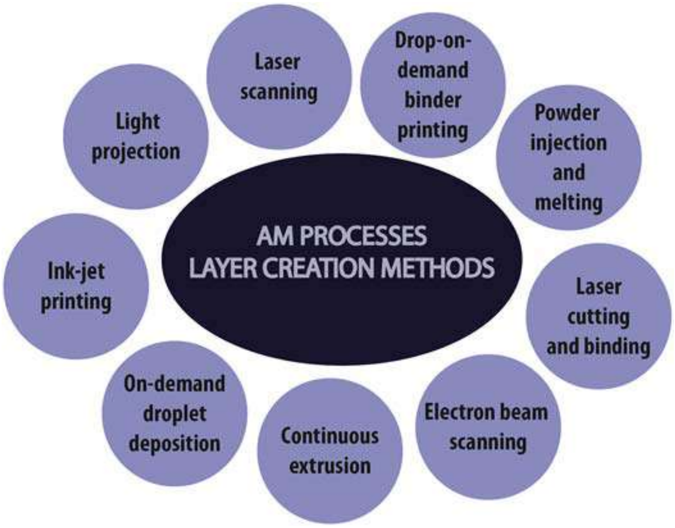

FIGURE 3.2 Classification of additive manufacturing processes due to the method of layer application and fixation.

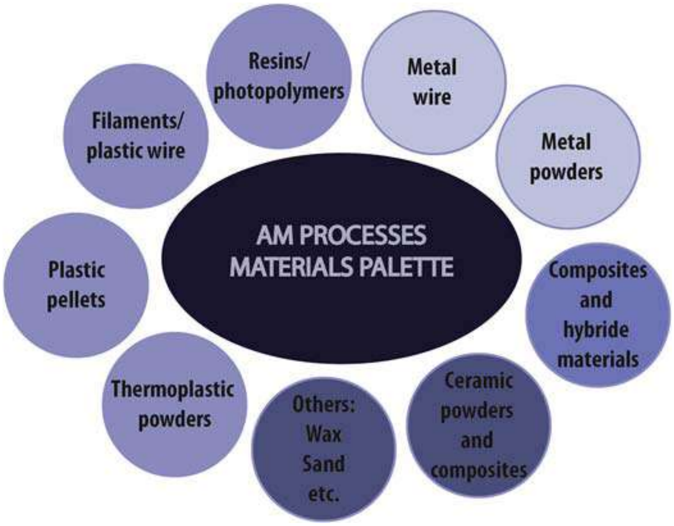

FIGURE 3.3 Classification of additive manufacturing processes by the type of material used in the process.

3.2 Brief description of additive manufacturing processes

3.2.1 *Binder jetting*

BJT is a process in which powder materials are bonded using a selectively sprayed liquid bonding agent [1]. After the printing process is completed, usually the models require curing and then sintering to give them the desired density and appropriate mechanical and strength properties [11,12].

The BJT process was developed in 1993 by researchers at MIT (Massachusetts Institute of Technology), as a 3DP (Three-Dimensional Printing) technology involving selective bonding of gypsum powder with a binder sprayed through a head similar to that of an inkjet printer. Over time, the technology has evolved and now functions as a technology with the same name as the process, Binder Jetting.

The detailed process of making the model involves spreading a thin layer of powder (with a grain thickness of 5–30 μm) on the working platform of the device, and then selectively spraying with inkjet nozzles drops of binding agent (with a diameter of about 80 μm) and colored ink in the case of color printing, then moving the working platform down and applying another layer of powder and repeating the process until the finished object is obtained. After the printing process is completed, the model in the powder layer is fixed by heating the container with the entire content, and only after fixing it is cleaned of powder residue and subjected to possible further finishing processes such as sintering, infiltration with metal (usually bronze) or acrylic (color prints), or covering with an additional layer of epoxy [10,13].

Printing is done primarily with metal powders (stainless steel, Inconel alloys, tungsten carbide) and quartz sand, but gypsum (sandstone) and polymer powders (PMMA) are also applicable. In case of sand used for casting molds, sintering in high-temperature furnaces is unnecessary. For full-color printing, sandstone and PMMA powders are used [14].

The main advantages of BJT technology are high quality and dimensional accuracy of prints, and high process efficiency of up to 40 kg/h possible, among other things, due to densification of models on the workspace and simultaneous printing of multiple models. This means that, for example, a 100-nozzle printhead can create parts at a speed of up to about 200 cm^3/min. It should be noted, however, that quality and dimensional accuracy are strongly dependent on powder quality and powder type. Fine-grained powders allow better results, but their application is more difficult, as they can be subject to caking and movement on the work table caused by head movements. The material also determines the typical layer height, which is 100 μm for full-color models, 50 microns for metal parts, and 200−400 μm for sand casting mold materials [15]. The quality of the model will not only be affected by the powder, but also by the binder, which must have very low viscosity, high shear stress, high stability, clean firing, be compatible with the powder, etc. Similarly, the primary particle bonding methods, which are classified as In-Liquid and In-Bed binding, will also affect the print. The limitation of the technology is also the surface finish of the metal parts, which even after finishing processes have porosity in the range of 3%−10%, making them unsuitable for high-performance applications [13,16].

3.2.2 Directed energy deposition

DED is a process where materials are melted during deposition using focused thermal energy. The energy source can be a laser beam, an electron beam, or a plasma arc. The deposited materials are in the form of wire or powder and are mainly metals (e.g., titanium and its alloys, inconel, tantalum, tungsten, niobium, stainless steel, aluminum, nickel, cobalt, tin, copper). DED also enables the fabrication of components with different compositions or hybrid structures consisting of multiple materials [1,11].

The DED technique involves applying layer upon layer of material to the base or component being repaired or according to a prepared model cut into layers. The material is applied through a nozzle mounted on a multiaxis arm (usually 4 or 5) and directly melted during deposition. This procedure is repeated many times until the layers solidify and the object is repaired or created [17].

DED processes are characterized by high yield. They are primarily applicable to the printing and repair of large industrial metal structures and components, especially for the aerospace sector, but can also be used to produce robust, lightweight composite parts. Different variations of DED technology are found under names such as Laser Engineered Net Shaping (LENS), Direct Metal Deposition (DMD), Electron Beam Additive Manufacturing (EBAM), WAAM, and polymer DED [18,19].

Polymer DED is a technology developed by AREVO dedicated to the production of composite parts. The material used for printing is wire or filament of carbon fiber impregnated with a thermoplastic polymer matrix. The carbon fiber content of the composite material is up to 50% of the material volume, which enables high strength parameters and low weight. A laser beam is used to deposit the material, and the special environment necessary for most processes with metals is not required. The material is melted at the same time as it is deposited by the nozzle [20,21].

DED technologies are used for the repair and manufacture of large-scale components, which involves much lower expectations of process precision compared to other three-dimensional (3D) printing technologies and much higher productivity and speed. The batch volume is above 1000 mm^3, the thickness of the print used is 1−3 mm, and the powder particle size is 50−150 μm. The parts produced require minimal tooling and relatively little postprocessing [18]. The resolution of the DED process depends on the energy source (laser > electron beam > electric arc), the more heat supplied the higher it is. The fabrication rate is a result of the material deposition rate and is about 0.5 kg/h for LENS technology, up to 9 kg/h for EBAM, and up to 10 kg/h for WAAM [19].

3.2.3 Material extrusion

MEX is a group of AM processes in which a material (mainly thermal plastics) is selectively applied layer by layer by being extruded through a nozzle. These include two commonly used equivalent technologies: Fused Deposition

Modeling (FDM) and Fused Filament Fabrication (FFF) (the former of which is patented by Stratasys Inc.), and the relatively new pellet extrusion printing technologies still in research and development, attracting increasing interest, which are known as Fused Granulate Fabrication (FGF), Fused Pellet Fabrication (FPF) or Fused Particle Fabrication, as well as the new powder melt extrusion (PME) technology and Direct Ink Writing (DIW) technology.

FDM/FFF technology relies on extrusion of the building material, which is the filament. Filament is a thermoplastic material wound onto a spool, usually with a diameter of 1.75 mm, or 2.85 mm or 3.00 mm. Filament is transported to the extruder and printhead, from which it is extruded in a semiliquid form, and after extruding to the work surface, it hardens almost immediately changing back into a solid form. The head temperature depends on the type of filament and is usually 190–280°C. The type of material used and the expected quality of the print has an impact on the choice of nozzle diameter used for extrusion (usually 0.4–0.6 mm for polymer composites). In most FDM/FFF printers, the printhead operates in the *X* and *Y* axis, while the work table operates in the *Z*-axis. After the printhead applies a layer, the table is lowered and the next layer is extruded, an action that is repeated until the entire model is achieved [22–24].

FGF/FPF technologies use a thermoplastic pellet instead of a filament, which is heated in a barrel and screw extrusion system and then extruded through a nozzle analogous to FDM/FFF technology [25–29]. Powder can also be extruded in a similar manner as pellets, which is the case in PME technology [30].

Extrusion-based technologies are currently the most widely used. The process is constantly being refined and improved, and new materials are being introduced to the market. The design of devices working with this technology is very simple, making them affordable. Low cost devices working with this technology are available for as little as a few hundred Euros and are commonly used by hobbyists and educational institutions. A wide industrial range of applications, on the other hand, is made possible by a very good availability of a variety of materials, where the machines are used to produce durable structural parts from materials such as ULTEM and PEEK [11,31].

Both FFF and FGF technologies use thermoplastic polymers as materials. In the case of FFF, these are processed into filament form before being delivered to the 3D printer, which can affect the properties of the material and increase its price. The advantage of FGF is the use of the material in the form of unprocessed pellets, which also creates the possibility of combining/mixing different materials directly in the 3D printing process, as well as the use of materials that are not suitable for the production of filament, or are difficult to print in this form (e.g., EVA, PVDF). The resolution in FGF printing is much lower than in FFF. This is related to the height of the printed layer, which for FGF is 1–5 mm, while for FFF is 0.1–0.4 mm. Comparing the productivity, it is much higher for FGF technology than FFF and ranges from 227 g/h to 9 kg/h and from 2.27 g/h to 113 g/h, respectively. In FFF printing, the productivity is limited by the size of the heating zone, while in FGF it is limited by the extruder size and screw design. Therefore, FGF is recommended for printing larger parts not requiring particularly high quality or flexible parts, while FFF is recommended for smaller parts with greater detail [27,28,31–33].

Direct Ink Writing (DIW) technology (also called Robocasting), on the other hand, involves extruding the liquid-phase ink through small nozzles with controlled flow under pressure and depositing paths of this material layer by layer to produce a 3D model. DIW is widely used at the meso- and microscale. It has applications for architectural design, aerospace engineering [34], or ceramics [35], but also for 4D printing especially of shape-changing materials in biomedicine or robotics. In addition to shape memory polymers, materials such as liquid crystal elastomers, hydrogels, composites, ferromagnetic domains, and bioactive glasses, among others, are applicable in this technology. The quality of DIW prints depends primarily on the specific rheological parameters of the ink, precise regulation on its viscosity. The main advantages of the technology are: the possibility of free selection of materials including nanocomposites with different contents of nanofillers or nanoparticles, and the possibility of multimaterial printing, as well as the possibility of obtaining high printing resolution due to the use of microdisks, and low printing cost due to the simplicity of the printing device, which can even be self-constructed [36–38].

3.2.4 *Material jetting*

MJT is the process of creating a model from droplets of a liquid material such as photopolymer resin or wax. The material is selectively sprayed onto the work platform using a nozzle and fixed immediately after application. The model is created layer by layer by moving the work platform down in the *Z*-axis. In the case of polymers, UV light emitted from a lamp integrated into the printhead is used for fixation. In general, the process resembles traditional 2D inkjet printing [1,4,11].

Different variations of the MJT process are available on the market: PolyJet (from Objet company) and Multi Jet Printing (MJP from 3D Systems), where the model is created from thermoset photopolymers (acrylics), and DOD (Drop-On-Demand), where the model is created from wax (from Solidscape company), or ceramic NPJ (NanoParticle Jetting from XJet).

Models created using MJT processes are characterized by a smooth surface finish, high dimensional accuracy, and uniform mechanical and thermal properties. Printing can be performed using a wide range of materials with very different properties, such as: touch resin (ABS-like), durable resin (PP-like), clear resin, rubber-like resin, heat-resistant resin, ceramic filled resin, castable resin, dental resin, and wax. This makes MJT widely applicable.

In the MJT process, the material is applied continuously by parallel printing heads, which makes it possible to produce multimaterial and multicolor prints, as well as prints with different glosses (glossy and matte). More complex models require the use of supports, which are produced in parallel with the printing process by applying a soluble, easily removable support material next to the actual material.

The layer height in MJ depends on the type of material used for printing and is typically 16–32 μm. Printing parameters due to the nature of the process (complex physics of droplet formation) are largely set by the machine manufacturer [39].

3.2.5 Powder bed fusion

PBF involves selective fusion of powder using thermal energy [1]. The fusion of metal powder, polymer powder, or alloys is performed using a laser, an electron beam, a heated thermal printhead, or an intense light source and mask, depending on the technology used [4,11,17]. Among PBF processes, there are several 3D printing technologies under different names: Selective laser sintering (SLS), Selective laser melting (SLM), Simultaneous Intensity-Selective Laser Sintering (SI-SLS), Selective heat sintering (SHS), Laser powder bed fusion (LPBF), Direct metal laser sintering (DMLS), Direct metal laser melting (DMLM), Electron beam melting (EBM), and Multi Jet Fusion (MJF).

SLS, SI-SLS, SHS, and MJF will be discussed in more detail as these techniques use polymer powders as materials, other technologies are dedicated to metal powders. Among polymer powders the most commonly used are polyamide powders (mainly PA12 and to a lesser extent PA11), but also polystyrene (PS) powders, thermoplastic elastomers (TPEs), and polyaryletherketones (PAEKs) are used.

SLS involves the targeted sintering of polymer powders using a laser. The powder particles are combined by melting rather than fusing. The technology is useful for mass production of single-material products [40]. In detail, the process involves depositing a thin layer of powder (typically 0.1 mm) on a platform, where a laser beam is then used to selectively sinter the powder. Once the entire surface has been scanned, the platform is moved down and another layer of powder is applied to be selectively sintered. The process is repeated layer by layer until the finished product is achieved. Due to the creation of a powdered model that supports individual components, no support is required regardless of its design [23,41].

SLS technology allows the creation of single-material models only. An alternative method that enables the fabrication of multimaterial components is SI-SLS of polymer powders. In this technology, different powder materials that can have different optical and thermal properties are processed simultaneously. Two different powder materials are deposited side by side using vibrating nozzles and are then selectively heated at the same time, with different preheating temperatures locally determined for different areas of the material with different melting points. After both polymers are heated to their preheating temperatures, they are simultaneously melted by the Thulium laser and the micromirror array. After both materials are molten, the device platform is lowered and the process is repeated for the next layer until the entire model is produced [40,42].

SHS technology was developed in 2011 as an alternative to SLS technology, where the processes that sinter powder or fuse it without reaching melting temperatures are performed using a desktop device equipped with a thermal head rather than a laser. This process is less efficient and less intensive, but more scalable. It is primarily used in thermoplastic prototype manufacturing.

MJF technology was patented in 2015 by HP and is significantly different from other powder technologies. Namely, it combines PBF elements with 2D inkjet printing. A layer of polymer powder (primarily PA12 is used, but the range of materials is expanding to include PA11 or TPU) is applied to a substrate, onto which moving inkjet heads spray two types of agent. These are fixing agent (fusing agent) and detailing agent (detailing agent), respectively. An infrared heating device then moves over the layer and melts the powder with the applied fusing agent. In color printers, there are additionally four heads with colored ink, allowing to obtain multicolored printouts. The process is repeated for successive layers, and then, as in other powder technologies, the unbound powder that supports the model is removed. The main advantage of MJF technology over SLS is its efficiency and productivity and the possibility of creating multicolor prints. The time to produce a prototype is up to 10 times shorter with MJF compared to SLS. Besides, the technology allows better use of powder recovered from the previous process (the recommendation is to recycle at most 70% of the used powder) [43–47].

3.2.6 *Sheet lamination*

SHL involves creating a spatial model from sheets of material that are cut and joined together, with the cutting occurring before or after the material is joined, depending on the technology [1,11]. SHL processes include Laminated Object Manufacturing (LOM), Computer-aided Manufacturing of Laminated Engineering Materials (CAM-LEMs), Selective Deposition Lamination (SDL), Ultrasonic Additive Manufacturing (UAM), and Selective Lamination Composite Object Manufacturing (SLCOM) technologies. LOM technology can use sheets of plastic, or paper, as well as fabrics, composites, and sheets [48,49]. CAM-LEM, on the other hand, uses polymer tapes, partially filled with ceramic particles (casted green preceramic tapes), or metal foils [49]. In SDL, sheets of paper are joined together, and unlike LOM, adhesive is applied only to the part of the sheet that will form the object [50]. UAM, on the other hand, uses metal sheets or webs that are bonded together using ultrasonic welding [51,52]. In SLCOM, woven fiber composites preimpregnated with thermoplastics matrix are used [53].

In LOM technology, the sheet is fed to a work table where the layers are joined and cut out. The technology where the layers are first laminated and then cut (called “bond-then-cut” or “cut-on-the-stack” method) is more precise and eliminates some of the possible errors; moreover it allows the use of excess material as support structures (supports). LOM, where the “cut-then-bond” method is used, is called CAM-LEM. The sheets are cut using a laser or possibly a numerically controlled knife. The layers of material are joined together by laminating—bonding by means of an adhesive layer or one of the materials may already contain an applied adhesive. The sheets are pressed together using a roller, which can be heated to activate the adhesive. The finished spatial model is obtained by repeatedly lowering the table by the thickness of the sheet and repeating the process [49,54].

The undoubted advantage of the technologies constituting the group of SHL processes is the possibility of processing a wide range of materials. In addition, among the advantages are the fairly low cost of obtaining a prototype due to the cost of the material especially when using paper and the fact that the models are durable and robust and can be processed (e.g., drilling, grinding, painting), and in the case of those made of plastic or paper they are flexible. However, the quality of the resulting models may not be satisfactory due to the stepping effect resulting from the combination of successive overlapping layers. Although it can be reduced by introducing special methods of cutting sheets (at a slant, using laser), nevertheless, it is characteristic of this process. Moreover, poor control of the laser beam can cause penetration into previously cut layers and lead to dimensional instability. Another limitation is the inability to produce parts with internal cavities. Another significant problem is the material waste created during the cutting process and the high energy consumption, making SHL processes of limited application [48,50].

3.2.7 *Vat photopolymerization*

VPP is a process in which a liquid photopolymer is selectively cured in a vat. The polymerization is activated by UV or visible light, depending on the technology and the photopolymer being cured, and leads to the formation of a solid by cross-linking polymer resins [1,11,55,56].

Among the VPP processes, the following technologies are distinguished: Stereolithography (SLA), Digital Light Processing (DLP), Continuous Digital Light Processing (CDLP), Continuous Liquid Interface Production (CLIP), Digital Light Synthesis (DLS), Scan, Spin, and Selectively Photocure (3SP), Two-Photon Lithography (the abbreviations 2PL and TPL used interchangeably), Multiphoton Polymerization (2PP), Multiphoton Absorption Polymerization (MAP), and Direct Laser Writing (DLW). Depending on the method, the resin is cured by laser (SLA, 3SP, 2PL/2PP/DLW), digital projection (DLP), light emitting diode (LED), and oxygen (CDLP/CLIP/DLS). Models are created from liquid photo-curable resins such as epoxy, polyurethane, polyester, and acrylic resin. In VPP technologies, more complex models require support structures to support the engineered product [5,55,57–59].

Stereolithography is the oldest method of VPP processes, as well as all AM processes. The model is produced using a computer-controlled laser beam (usually low power). The liquid resin filling the vessel of the moving platform is polymerized upon contact with an electromagnetic wave of the appropriate wavelength, after which the platform is lowered by a distance equal to the thickness of the fused layer. The process is repeated until the finished model is obtained. Production accuracy is related to the diameter of the laser beam at the curing point, i.e., the quality depends on the spot size. 3SP technology is a variation of SLA technology, where the resin curing is faster by using a rotating mirror and laser. In SLA, the layer height varies from 12 to 150 μm, with 100 μm typically being used. The print speed of standard SLA printers is in the range of 10–20 mm/h. The main advantages of SLA technology are high dimensional accuracy and smooth surface finish. The major disadvantages include the need for support structures, high cost, and limited resin availability [48,55].

DLP technology differs from SLA only in the method of curing the photopolymer. Instead of a laser beam, a digital light projector is used that cures the entire layer at once, layer by layer, making the method much faster but less accurate. However, the accuracy of object fabrication and the possible pixelation effect of the layer depend on the resolution of the projector. Moreover, in DLP, the irradiation of large areas can cause unwanted resin shrinkage, which does not occur with spot irradiation. For this reason, the DLP method is mostly used for small projects where there are no large areas in a single layer [55,60].

CDLP technology is also called CLIP or DLS. It works on a similar principle to DLP technology, i.e., using digital projection, but the LED projection is done using an oxygen permeable window rather than a regular glass window and is done continuously rather than layer by layer. The dead zone created above the oxygen permeable window maintains a constant fluid level, which helps in the continuous production of the required geometry. This reduces the risk of print breaks due to peel forces and increases print resolution. Since the exposure is continuous, the object fabrication process is much faster than in DLP or SLA and the problem of layer merging is eliminated. CDLP allows prototypes to be printed at speeds of several hundred millimeters per hour [55,59,61,62].

VPP processes also include technologies that are DLW methods appearing under the names Two-Photon Lithography, 2PP, MAP, or Multiphoton Lithography. These technologies are dedicated to the fabrication of micro- and nanostructures. It exploits the nonlinear dependence of polymerization rate on irradiating light intensity to produce true 3D structures with element sizes exceeding the diffraction limit. The smallest 3D ellipsoidal point obtained is called a voxel (volume pixel) [63–67].

3.2.8 *AM hybrid technologies*

The development of new technologies and improvement of existing ones, new directions of research and applications create the need to explore new areas and to combine AM technologies with other processes in order to obtain new application areas. Hybrid additive technologies are only at the beginning of their research and development, but undoubtedly should be given attention as one of the further research directions [3,68]. Hybrid AM refers to both hybrid processes and machines as well as multimaterial, multistructured, and multifunctional printing. The main goal of most hybrid AM processes is to improve part quality and yield [69]. Fig. 3.4 shows the classification of hybrid AM processes [70].

3.3 Comparison of key techniques

3.3.1 *Surface quality*

The surface quality of printed models is closely related to the thickness of the applied layers and the form of the material. The thinner the layer, the smoother the surface and less visible "jaggedness" of the layers. PBF, BJT, and VPP processes allow the use of thin layers (about 0.1 mm), and MJT even thinner (about 0.02 mm). For SHL processes

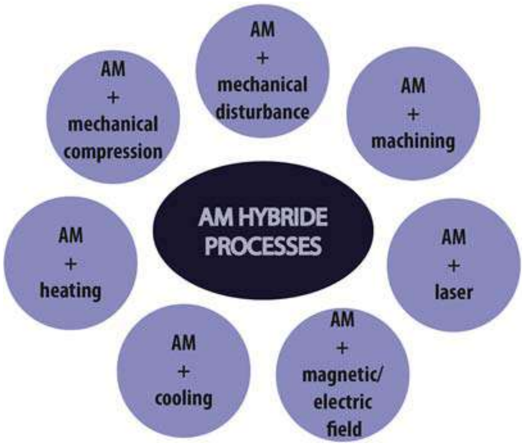

FIGURE 3.4 Classification of hybrid additive manufacturing processes.

the layer thickness depends on the material thickness, while in MEX processes this thickness is much larger (0.2 mm or more), as in DED processes [9,71].

The surface of models obtained from materials in powder form (i.e., PBF, BJT processes) is rough [72]. In contrast, models made from resins in the VPP and MJT processes have very high smoothness.

3.3.2 *Printing resolution*

Resolution has a significant impact on print quality and functionality. It is closely related to the technology and the construction material used. The highest resolutions can be achieved in the MJT and VPP processes, intermediate resolutions in PBF, and the lowest resolutions in MEX, SHL, and DED, respectively. Thus, for MJT processes, the resolution is 10—28 μm, while for VPP processes the resolution for each technology will be 10—140 μm for SLA (depending on laser spot size), 10—50 μm for DLP, 75—100 μm for CLIP, and 0.1—0.5 μm for TPL, respectively. For powder processes, the resolution is highly dependent on the type of powder and its grain size and for SLS technologies (PBF processes) is 50—100 μm, while for BJT it is 15—100 μm. For technologies belonging to MEX processes, the resolutions will be as follows: FDM 100—200 μm, FFF 180—400 μm. Whereas for LOM technology (which is an example of SHL processes), the resolution is 200—300 μm [5,8,9,15,30,39,43,56].

3.3.3 *Dimensional accuracy and deformation of models*

One of the most accurate 3D printing technologies is MJP and PolyJet (MJT processes). SLA or MJF technologies also have high accuracy. MJT systems have a very high dimensional accuracy of ±0.1—0.2% with a typical lower limit of ±0.02—0.1 mm. For SLA and MJF, the dimensional accuracy is ±0.2% with a lower limit of ±0.2 mm, while for SLS technology it is ±0.3% (with a lower limit of ±0.3 mm). For FDM/FFF technology, dimensional accuracy is ±0.15—0.5% with a lower limit of ±0.2—0.5 mm.

Many 3D printing processes are implemented using high temperatures, which can cause problems with model warping (FDM, SLS, DMSL/SLM), model curling (SLA/DLP), or dimensional changes due to thermal effects on polymers [39]. In BJ technology, bonding takes place at room temperature, which eliminates such problems. However, the shrinkage of the material also in BJ must be taken into account at the stage of preparation for printing, due to the subsequent fixation and finishing processes performed immediately after printing, giving the appropriate strength properties to the models.

3.3.4 *Process performance and maximum printed object size*

The process yields for the selected technologies are, respectively: BJT to 40 kg/h, FGF to 9 kg/h, FFF to 0.113 kg/h, LENS to 0.5 kg/h, EBAM to 9 kg/h, WAAM to 10 kg/h. Fabrication speed is lowest for MEX processes and is 0.05 cm/h and for MJT and SHL processes (0.4 and 0.45 cm/h, respectively). It is slightly higher for VPP (1.5 cm/h) and BJT (0.27—1.9 cm/h), while it is highest for PBF (2.5 cm/h) and DED (4.4 cm/h)[19]. In the technologies belonging to BJT and PBF, it is possible to print multiple models at the same time, which makes it possible to efficiently fill almost the entire design volume of the machine. Therefore, these technologies are well suited for low- and medium-volume production, not just rapid prototyping. What's more, in PBF processes, MJF technology has higher productivity than SLS—the time to produce a prototype is up to 10 times shorter for MJF compared to SLS. Among the MEX processes, FGF enables printing larger parts than FFF or FDM.

The maximum size of the printed object depends on the printing technology used, and this also depends on the type of material and finish, and the device used for printing. More specifically, it is limited to printing objects no larger than the size allowed by the 3D printer build area, which is not synonymous with its maximum volume. The largest production volumes of machines occur for the BJ technology (up to 2200 × 1200 × 600 mm); however, for technological reasons the size of the parts is strongly limited. Build area is up to 914.4 × 609.6 × 914.4 mm for FDM, 736.6 × 635 × 533.4 mm for SLA, 330 × 330 × 508 mm for SLS, 381 × 279.4 × 381 mm for MJF, 482.6 × 381 × 177.8 mm for PolyJet. Nevertheless, it should be kept in mind that the production volume of the machine is not equivalent to the maximum size of the printed model, which as mentioned can be limited due to the process flow and materials used [15,73,74].

3.3.5 *Multimaterial and multicolor capability*

Most models made by 3D printing processes are single-color and one- or two-material. The exceptions to this are BJT and MJT, which produce multicolored models. On the other hand, the second material is used in MEX and BJT processes, where it is used as a support material with soluble properties, or as a binder for the process realization. Nevertheless, it is worth keeping in mind that in BJT processes, the use of powder and binder enables to obtain specific material compositions that are not possible or easy to achieve using direct methods.

3.3.6 *The need for supports and the problem of production waste*

An important aspect of 3D printing is the need for supports that require subsequent removal in finishing processes. What's more, their introduction and removal can often reduce the quality of the final print. Processes that do not require their use are BJT, PBF, and part of the SHL technology because the necessary support of elements is provided by powder or construction material used in the printing process. They allow the creation of very complex, arbitrarily shaped geometric structures [7].

Support structures can be made of the material from which the object is made or, for part of the technology, be made of another material. The material used to make support structures in MEX processes may be soluble or require mechanical removal, which generates waste. Solid waste is also generated from the removal of structures from SLA resin prints, among others. The support material can also no longer be used after the removal of support structures in SHL processes, which are part of the material from model production. In processes where the model is built from powder, the powder can be reused, but requires depending on the technology to be mixed with fresh material (virgin powder). At the same time MJF technology is more environmentally friendly than SLS—it allows to reuse as much as 70% of powder without affecting print quality, where in SLS a refresh rate of 50% virgin powder mixed with 50% recycled powder is recommended.

3.3.7 *Need for finishing processes*

Finishing processes (support removal, mechanical or chemical smoothing, surface grinding and polishing, local melting, gap filling, coating to improve adhesion between layers, varnishing, painting, metallizing, illumination, leaching, coloring, sintering, infiltration, etc.) to a greater or lesser extent are applicable to most 3D prints. They affect not only the aesthetics of the print but also the mechanical properties. BJT printing results in green parts that absolutely require finishing processes to give them the right mechanical properties. First, there is a step of removing residual powders and then densifying the structures [12]. Finishing processes in the form of rinsing and illumination are also necessary for VPP processes where photo-curable resins are used. Finishing processes are also necessary for all technologies where supports are used (e.g., SLA, FDM, LOM) for removal ([8,75].

3.4 Market share of each technology and forecast

Different sources and forecasts give different contributions of each technology in 3D printing with polymers. Nevertheless, according to the indicated main 3D printing processes currently used are MEX and VPP, with PBF, or rather SLS technology belonging to it, and VPP with SLA technology playing a special role for industrial applications [76–78].

According to a report by Grand View Research [77], stereolithography was the market leader in 2020, as in previous years, with a share of over 10% in global revenue. High potential and dynamic growth in market share in the coming years is seen and projected for DLP technology and MJT processes among polymer-based processes, while EBM and DMLS among processes using metals [77].

According to SmarTech forecasts, by 2027 dynamic development and growth for polymer-based 3D printing processes (at 20% technology share) will occur only for PBF processes. The use of other processes is expected to decline. The share of key technologies, namely, MEX and VPP from 41% to 31%, respectively, in 2017, will decrease to 31% and 25% in 2027. While the use of MJT and BJT processes will be reduced by 2% from 9% and 6%, respectively [76].

3.5 Summary

The base technologies for 3D printing with polymers are currently still the oldest methods, such as: FDM, SLA, and SLS; however, the development of new technologies is dynamic and important. The main factors contributing to the progress in this area is the search for cheaper, more efficient solutions and enabling the use of an even wider range of materials. Each of the available technologies has its limitations, but with a conscious choice of the method, it is possible to produce the desired prototype or small/medium batch production of products with satisfactory quality. Properly made decision will result in the fact that printed model will have a specific aesthetics, precision, appropriate mechanical, thermal, and optical properties, specific surface finish (glossy/matte, smooth/rough, multicolored/monochromatic, transparent/opaque, etc.), and will be printed in a specified time and at a specified cost of production.

References

[1] ISO/ASTM 52900:2015 Additive Manufacturing — General Principles — Terminology.
[2] M.D. Monzón, Z. Ortega, A. Martínez, F. Ortega, Standardization in additive manufacturing: activities carried out by international organizations and projects, Int. J. Adv. Manuf. Technol. 76 (2015) 1111–1121.
[3] O. Abdulhameed, A. Al-Ahmari, W. Ameen, S.H. Mian, Additive manufacturing: challenges, trends, and applications, Adv. Mech. Eng. 11 (2) (2019), https://doi.org/10.1177/1687814018822880.
[4] M. Kamran, A. Saxena, A comprehensive study on 3D printing technology, MIT Int. J. Mech. Eng. 6 (2) (2016) 63–69.
[5] S.C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, Polymers for 3D printing and customized additive manufacturing, Chem. Rev. 117 (2017) 10212–10290.
[6] M. Jiménez, L. Romero, I.A. Dominguez, M. del Mar Espinosa, M. Dominguez, Additive manufacturing technologies: an overview about 3D printing methods and future prospects, Complexity (2019) 30, https://doi.org/10.1155/2019/9656938. ID 9656938.
[7] J. Jiang, x. Xu, J. Stringer, Support structures for additive manufacturing: a review, J. Manuf. Mater. Process. 2 (64) (2018), https://doi.org/10.3390/jmmp2040064.
[8] J.R.C. Dizon, A.H. Espera Jr., Q. Chen, R.C. Advincula, Mechanical characterization of 3D-printed polymers, Addit. Manuf. 20 (2018) 44–67.
[9] The International Academy for Production Engineering, in: CIRP Encyclopedia of Production Engineering, CIRP, 2014, https://doi.org/10.1007/978-3-642-20617-7.
[10] I. Gibson, D. Rosen, B. Stucker, Additive Manufacturing Technologies. 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing, second ed., Springer Science+Business Media, New York, NY, 2015.
[11] D. Bourell, J.P. Kruth, M. Leu, G. Levy, D. Rosen, A.M. Beese, A. Clare, Materials for additive manufacturing, CIRP Ann. Manuf. Technol. 66 (2017) 659–681.
[12] H. Miyanaji, M. Orth, J.M. Akbar, L. Yang, Process development for green part printing using binder jetting additive manufacturing, Front. Mech. Eng. 13 (4) (2018) 504–512.
[13] M. Ziaee, N.B. Crane, Binder jetting: a review of process, materials, and methods, Addit. Manuf. 28 (2019) 781–801.
[14] O. Diegel, A. Nordin, D. Motte, A Practical Guide to Design for Additive Manufacturing, Springer Series in Advanced Manufacturing, Springer, 2020, https://doi.org/10.1007/978-981-13-8281-9_2.
[15] A.B. Varotsis, Introduction to binder jetting 3D printing, https://www.hubs.com/knowledge-base/introduction-binder-jetting-3d-printing/ (Accessed 16 June 2021).
[16] N. Shahrubudin, T.C. Lee, R. Ramlan, An overview on 3D printing technology: technological, materials, and applications, Proc. Manuf. 35 (2019) 1286–1296, https://doi.org/10.1016/j.promfg.2019.06.089.
[17] Y. Zhai, D.A. Lados, J.L. Lagoy, Additive manufacturing: making imagination the major limitation, J. Occup. Med. 66 (5) (2014) 808–816, https://doi.org/10.1007/s11837-014-0886-2.
[18] V. Carlota, The Complete Guide to Directed Energy Deposition (DED) in 3D Printing, 2019. https://www.3dnatives.com/en/directed-energy-deposition-ded-3d-printing-guide-100920194/#! (Accessed 10 September 2019).
[19] J.-Y. Lee, J. An, C.K. Chua, Fundamentals and applications of 3D printing for novel materials, Appl. Mater. Today 7 (2017) 120–133.
[20] L. Langnau, What Is Polymer Directed Energy Deposition (DED) for 3D Printing and How Can it Benefit You?, 2019. https://www.designworldonline.com/what-is-polymer-directed-energy-deposition-ded-for-3d-printing-and-how-can-it-benefit-you/ (Accessed 26 June 2019).
[21] D. Zhang, N. Rudolph, P. Woytowitz, Reliable Optimized Structures with High Performance Continuous Fiber Thermoplastic Composites from Additive Manufacturing, SAMPE, 2019 (Conference).
[22] J.I. Aguilar-Duque, J.L. Hernández-Arellano, L. Avelar-Sosa, G. Amaya-Parra, U.J. Tamayo-Pérez, Chapter 16. Additive manufacturing: fused deposition modeling advances, in: J.L. García Alcaraz, et al. (Eds.), Best Practices in Manufacturing Processes, Springer Nature Switzerland AG, Cham, 2019.
[23] A.D. Valino, J.R.C. Dizon, A.H. Espera Jr., Q. Chen, J. Messman, R.C. Advincula, Advances in 3D printing of thermoplastic polymer composites and nanocomposites, Prog. Polym. Sci. 98 (2019) 101162, https://doi.org/10.1016/j.progpolymsci.2019.101162.
[24] A. Ambrosi, M. Pumera, 3D-printing technologies for electrochemical applications, Chem. Soc. Rev. 45 (2016) 2740–2755.
[25] J. Marchewka, J. Laska, Processing of poly-L-lactide and poly(L-lactide-co-trimethylene carbonate) blends by fused filament fabrication and fused granulate fabrication using RepRap 3D printer, Int. J. Adv. Manuf. Technol. 106 (2020) 4933–4944, https://doi.org/10.1007/s00170-020-04981-z.

[26] A. Alexandre, F.A.C. Sanchez, H. Boudaoud, M. Camargo, J.M. Pearce, Mechanical properties of direct waste printing of polylactic acid with Universal pellets extruder: comparison to fused filament fabrication on open-source desktop three-dimensional printers, 3D Print. Addit. Manuf. 7 (5) (2020), https://doi.org/10.1089/3dp.2019.0195.

[27] N. Kumar, P.K. Jain, P. Tandon, P.M. Pandey, The effect of process parameters on tensile behavior of 3D printed flexible parts of ethylene vinyl acetate (EVA), J. Manuf. Process. 35 (2018) 317–326.

[28] N. Kumar, P.K. Jain, P. Tandon, P.M. Pandey, Investigation on the effects of process parameters in CNC assisted pellet based fused layer modeling process, J. Manuf. Process. 35 (2018) 428–436, https://doi.org/10.1016/j.jmapro.2018.08.029.

[29] S. Liu, P. Zhao, S. Wu, C. Zhang, J. Fu, Z. Chen, A pellet 3D printer: device design and process parameters optimization, Adv. Polym. Technol. (2019) 8, https://doi.org/10.1155/2019/5075327. ID 5075327.

[30] B.M. Boyle, P.T. Xiong, T.E. Mensch, T.J. Werder, G.M. Miyake, 3D printing using powder melt extrusion, Add. Manuf. 29 (2019) 100811, https://doi.org/10.1016/j.addma.2019.100811.

[31] L. Yang, K. Hsu, B. Baughman, D. Godfrey, F. Medina, M. Menon, S. Wiener, Introduction to additive manufacturing, in: Additive Manufacturing of Metals: The Technology, Materials, Design and Production. Springer Series in Advanced Manufacturing, Springer, Cham, 2017, https://doi.org/10.1007/978-3-319-55128-9_1.

[32] G. Costantino, Z. DiVencenzo, 3D Printing with Fused Filament Fabrication and Fused Granulate Fabrication (Pellet Printing), https://www.dsm.com/additive-manufacturing/en_US/insights/blog/3d-printing-with-fused-filament-fabrication-and-fused-granulate-fabrication.html (Accessed 10 June 2021).

[33] S. Whyman, K.M. Arif, J. Potgieter, Design and development of an extrusion system for 3D printing biopolymer pellets, Int. J. Adv. Manuf. Technol. 96 (2018) 3417–3428.

[34] Q. Sun, J. Liu, H. Cheng, Y. Mou, J. Liu, Y. Peng, M. Chen, Fabrication of 3D structures via direct ink writing of kaolin/graphene oxide composite suspensions at ambient temperature, Ceram. Int. 45 (15) (2019) 18972–18979, https://doi.org/10.1016/j.ceramint.2019.06.136.

[35] E. Ordoñez, J.M. Gallego, H.A. Colorado, 3D printing via the direct ink writing technique of ceramic pastes from typical formulations used in traditional ceramics industry, Appl. Clay Sci. 182 (2019) 105285, https://doi.org/10.1016/j.clay.2019.105285.

[36] H.Q. Wei, Q.W. Zhang, Y.T. Yao, L.W. Liu, Y.J. Liu, J.S. Leng, Direct-write fabrication of 4D active shape-changing structures based on a shape memory polymer and its nanocomposite, ACS Appl. Mater. Interfaces 9 (2017) 876–883.

[37] L. Li, Q. Lin, M. Tang, A.J.E. Duncan, C. Ke, Advanced polymer designs for direct-ink-write 3D printing, Chem. Eur J. 25 (2019) 10768–10781.

[38] X. Wan, L. Luo, Y. Liu, J. Leng, Direct ink writing based 4D printing of materials and their applications, Adv. Sci. 7 (16) (2020), https://doi.org/10.1002/advs.202001000.

[39] A.B. Varotsis, Introduction to material jetting 3D printing, https://www.hubs.com/knowledge-base/introduction-material-jetting-3d-printing/ (Accessed 20 June 2021).

[40] T. Stichel, T. Brandl, T. Hauser, B. Geißler, S. Roth, Electrophotographic multi-material powder deposition for additive manufacturing, 10th CIRP conference on photonic technologies [LANE 2018], Proc. CIRP 74 (2018) 249–253.

[41] K. Wudy, L. Lanzl, D. Drummer, Selective leser sintering of filled polymer systems: bulk properties and laser beam material interaction, Phys. Proc. 83 (2016) 991–1002.

[42] T. Stichel, T. Laumer, M. Raths, S. Roth, Multi-material deposition of polymer powders with vibrating nozzles for a new approach of laser sintering, JLMN J. Laser Micro Nanoeng. 13 (2) (2018) 55–62.

[43] S. Morales-Planas, J. Minguella-Canela, J. Lluma-Fuentes, J.A. Travieso-Rodriguez, A.-A. García-Granada, Multi jet fusion PA12 manufacturing parameters for watertightness, strength and tolerances, Materials 11 (8) (2018) 1472, https://doi.org/10.3390/ma11081472.

[44] H.J. O'Connor, A.N. Dickson, D.P. Dowling, Evaluation of the mechanical performance of polymer parts fabricated using a production scale multi jet fusion printing process, Addit. Manuf. 22 (2018) 381–387, https://doi.org/10.1016/j.addma.2018.05.035.

[45] F. Calignano, F. Giuffrida, M. Galati, Effect of the build orientation on the mechanical performance of polymeric parts produced by multi jet fusion and selective laser sintering, J. Manuf. Process. 65 (2021) 271–282, https://doi.org/10.1016/j.jmapro.2021.03.018.

[46] C. Pandelidi, K.P.M. Lee, M. Kajtaz, Effects of polyamide-11 powder refresh ratios in multi-jet fusion: a comparison of new and used powder, Addit. Manuf. 40 (2021) 101933, https://doi.org/10.1016/j.addma.2021.101933.

[47] C. Cai, W.S. Tey, J. Chen, W. Zhu, X. Liu, T. Liu, L. Zhao, K. Zhou, Comparative study on 3D printing of polyamide 12 by selective laser sintering and multi jet fusion, J. Mater. Process. Technol. 288 (2021) 116882, https://doi.org/10.1016/j.jmatprotec.2020.116882.

[48] M. Schmidt, M. Merklein, D. Bourell, D. Dimitrov, T. Hausotte, K. Wegener, L. Overmeyer, F. Vollertsen, G.N. Levy, Laser based additive manufacturing in industry and academia, CIRP Ann. Manuf. Technol. 66 (2017) 561–583.

[49] B. Dermeik, N. Travitzky, Laminated object manufacturing of ceramic-based materials, Adv. Eng. Mater. 22 (9) (2020), https://doi.org/10.1002/adem.202000256.

[50] C.M. Thakar, S.P. Deshmukh, T.A. Mulla, A review on selective deposition lamination 3D printing technique, Int. J. Adv. Sci. Res. Eng. Trends 4 (8) (2019-2020) 7–11.

[51] A. Levy, A. Miriyev, N. Sridharan, T. Han, E. Tuval, S.S. Babu, M.J. Dapino, N. Frage, Ultrasonic additive manufacturing of steel: method, post-processing treatments and properties, J. Mater. Process. Technol. 256 (2018) 183–189, https://doi.org/10.1016/j.jmatprotec.2018.02.001.

[52] A. Hehr, M. Norfolk, A comprehensive review of ultrasonic additive manufacturing, Rapid Prototyp. J. 26 (3) (2020) 445–458, https://doi.org/10.1108/RPJ-03-2019-0056.

[53] V. Dikshit, G.D. Goh, A.P. Nagalingam, G.L. Goh, W.Y. Yeong, Chapter 17 – Recent progress in 3D printing of fiber-reinforced composite and nanocomposites, in: B. Han, S. Sharma, T.A. Nguyen, L. Longbiao, K.S. Bhat (Eds.), In Micro and Nano Technologies, Fiber-Reinforced Nanocomposites: Fundamentals and Applications, Elsevier, 2020, pp. 371–394, https://doi.org/10.1016/B978-0-12-819904-6.00017-7.

[54] J. Park, M.J. Tari, H.T. Hahn, Characterization of the laminated object manufacturing (LOM) process, Rapid Prototyp. J. 6 (1) (2000) 36–50, https://doi.org/10.1108/13552540010309868.

[55] M. Pagac, J. Hajnys, Q.-P. Ma, L. Jancar, J. Jansa, P. Stefek, J. Mesicek, A review of vat photopolymerization technology: materials, applications, challenges, and future trends of 3D printing, Polymers 13 (4) (2021) 598, https://doi.org/10.3390/polym13040598.

[56] C. Armstrong, How to design parts for SLA 3D printing, https://www.hubs.com/knowledge-base/how-design-parts-sla-3d-printing/ (Accessed 20 June 2021).

[57] F. Honarvar, A. Varvani-Farahani, A review of ultrasonic testing applications in additive manufacturing: defect evaluation, material characterization, and process control, Ultrasonics 108 (2020) 106227, https://doi.org/10.1016/j.ultras.2020.106227.

[58] A. Bagheri, J. Jin, Photopolymerization in 3D printing, ACS Appl. Poly. Mater. 1 (4) (2019) 593–611, https://doi.org/10.1021/acsapm.8b00165.

[59] R. Hu, B. Huang, Z. Xue, Q. Li, T. Xia, W. Zhang, C. Lu, H. Xu, Synthesis of photocurable cellulose acetate butyrate resin for continuous liquid interface production of three-dimensional objects with excellent mechanical and chemical-resistant properties, Carbohydr. Polym. 207 (2019) 609–618, https://doi.org/10.1016/j.carbpol.2018.12.026.

[60] M. Monzón, Z. Ortega, A. Hernández, R. Paz, F. Ortega, Anisotropy of photopolymer parts made by digital light processing, Materials 10 (64) (2017) 1–15.

[61] R.V. Pazhamannil, P. Govindan, Current state and future scope of additive manufacturing technologies via vat photopolymerization, Mater. Today Proc. 43 (1) (2021) 130–136, https://doi.org/10.1016/j.matpr.2020.11.225.

[62] A. Redmann, P. Oehlmann, T. Scheffler, L. Kagermeier, T.A. Osswald, Thermal curing kinetics optimization of epoxy resin in digital light synthesis, Addit. Manuf. 32 (2020) 101018, https://doi.org/10.1016/j.addma.2019.101018.

[63] V. Harinarayana, Y.C. Shin, Two-photon lithography for three-dimensional fabrication in micro/nanoscale regime: a comprehensive review, Opt Laser. Technol. 142 (2021) 107180, https://doi.org/10.1016/j.optlastec.2021.107180.

[64] T. Baldacchini (Ed.), Micro and Nano Technologies, Three-Dimensional Microfabrication Using Two-Photon Polymerization, second ed., William Andrew Publishing, 2020.

[65] L. Li, J.T. Fourkas, Multiphoton polymerization, Mater. Today 10 (6) (2007) 30–37, https://doi.org/10.1016/S1369-7021(07)70130-X.

[66] D.M. Zuev, A.K. Nguyen, V.I. Putlyaev, R.J. Narayan, 3D printing and bioprinting using multiphoton lithography, Bioprinting 20 (2020), https://doi.org/10.1016/j.bprint.2020.e00090.

[67] A.T. Alsharhan, O.M. Young, X. Xu, A.J. Stair, R.D. Sochol, Integrated 3D printed microfluidic circuitry and soft microrobotic actuators via in situ direct laser writing, J. Micromech. Microeng. 31 (4) (2021) 044001.

[68] L. Chong, S. Ramakrishna, S. Singh, A review of digital manufacturing-based hybrid additive manufacturing processes, Int. J. Adv. Manuf. Technol. 95 (2018) 2281–2300.

[69] M.P. Sealy, G. Madireddy, R.E. Williams, P. Rao, M. Toursangsaraki, Hybrid processes in additive manufacturing, J. Manuf. Sci. Eng. 140 (6) (2018) 060801 (13 pages).

[70] S. Webster, H. Lin, F.M. Carter III, K. Ehmann, J. Cao, Physical mechanisms in hybrid additive manufacturing: a process design framework, J. Mater. Process. Technol. 291 (2021) 117048.

[71] S. Killi (Ed.), Additive Manufacturing: Design, Methods, and Processes, Pan Stanford Publishing, Singapore, 2017.

[72] W. Gao, Y. Zhang, D. Ramanujan, K. Ramani, Y. Chen, C.B. Williams, C.C.L. Wang, Y.C. Shina, S. Zhang, P.D. Zavattieri, The status, challenges, and future of additive manufacturing in engineering, Comput. Aided Des. 69 (2015) 65–89.

[73] Xometry, Tolerances and Build Area for 3D Printed Plastics, 2021, https://support.xometry.com/hc/en-us/articles/217170527-Tolerances-and-Build-Area-for-3D-Printed-Plastics (Accessed 12 July 2021).

[74] I. Jasiuk, D.W. Abueidda, C. Kozuch, S. Pang, F.Y. Su, J. Mckittrick, An overview on additive manufacturing of polymers, J. Occup. Med. 70 (3) (2018) 275–283.

[75] K. Govil, V. Kumar, D.P. Pandey, R. Praneeth, A. Sharma, Additive Manufacturing and 3D Printing: A Perspective, Advances in Engineering Design, Springer Nature Singapore Pte Ltd, 2019, https://doi.org/10.1007/978-981-1.

[76] SmarTech Publishing, Additive Manufacturing with Polymers and Plastics 2018, 2018, https://www.smartechanalysis.com/wp-content/uploads/2018/07/2018-polymers-pr-chart.png (Accessed 06 July 2021).

[77] Grand View Research, report3D Printing Market Size, Share & Trends Analysis Report By Component, By Printer Type (Desktop, Industrial), By Technology, By Software, By Application, By Vertical, By Material, By Region, And Segment Forecasts, 2021–2028, 2021, https://www.grandviewresearch.com/industry-analysis/3d-printing-industry-analysis (Accessed 06 July 2021).

[78] L. Columbus, The State of 3D Printing, 2018. https://www.forbes.com/sites/louiscolumbus/2018/05/30/the-state-of-3d-printing-2018/?sh=7e762d87b0a8 (Accessed 30 May 2018).

C H A P T E R

4

Materials for 3D printing

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4.1 Introduction

For additive manufacturing (AM) (3D printing), polymers, metals, ceramics, and composites are used (see Chapter 3, Fig. 3.3). Considering the annual material usage, polymers are the main group of materials used in AM. They are available in various forms, namely as: liquid polymers (resins and binders), powders, pellets, filaments (wire), and films. The wide range of their types that are available and used is also very significant and ranks them as the most employed group of materials. Thermoplastics, thermosets, elastomers, hydrogels, polymer blends, biological systems, and polymer-based composites are used in AM [1–3].

The choice of the type of polymer depends on the chosen AM technology and the application of the object made of it, whether it is a finished product or a test prototype, which is related to the expected mechanical, chemical, and aesthetic properties of the made object. The most widespread applications are thermoplastics and thermoplastic composites, which are used in AM techniques such as SLA, SLS, MJF, and FDM/FFF, both for finished products and test prototypes [4].

Thermoplastics are plastics that can be processed repeatedly (but with a loss of certain properties in the subsequent processing), that become liquid under certain conditions (temperature and pressure), and that can be extruded or injected. They have good mechanical and chemical properties and good abrasion and impact resistance. However, their mechanical properties are low compared to common engineering materials. Nevertheless, the mechanical properties of thermoplastics can be improved by filling them with carbon, glass, or other additives – hence the use of thermoplastic composites is increasing. The most common thermoplastics are PLA, ABS, and PETG, while industrial applications include nylon (PA) and elastomers (TPU) [5,6].

Thermoplastic elastomers (TPEs) bridge the gap between soft rubber and hard plastic as they combine the characteristics of these two such different materials, namely flexibility and fairly good mechanical strength. Examples of TPEs include polyurethanes, styrene triblock copolymers (poly(styrene-butadiene-styrene), poly(styrene-isoprene-styrene)), and polyester elastomers [7–9].

Thermosetting plastics belong to duroplastics, which irreversibly change their shape during the curing process. They are materials in viscous or solid but soft form that are cured by heating or irradiation. These include photopolymer resins used in AM processes. Objects made from thermosetting plastics generally have higher quality and aesthetics than those made from thermoplastics. Their surface is smooth, as in injection molding, and they have high stiffness. A limitation when using them in functional applications may be the relatively high brittleness of most thermosets [10].

According to Jabil report "3D Printing Technology Trends" and statista reports polymers were the most widely used material among 3D printing users in 2017–2020 and continue to be in 2021 [11–13]. Also according to Wohlers Report [14] and Smartech [15], polymers represent the largest and most diverse group of materials for AM. 85.5% of the materials used in AM technologies are polymers, while metals account for 11.5% [14]. With photopolymers being the main group of polymers with a share of 56% in 2018, followed by polymeric powders (21%), while filaments have the smallest share (21%). The use of each group of polymeric materials has followed a similar trend in earlier years (in 2015 according to Wohlers Report data it was 45.5%, 24.9%, and 15.1%, respectively) and this is forecast to continue (Fig. 4.1).

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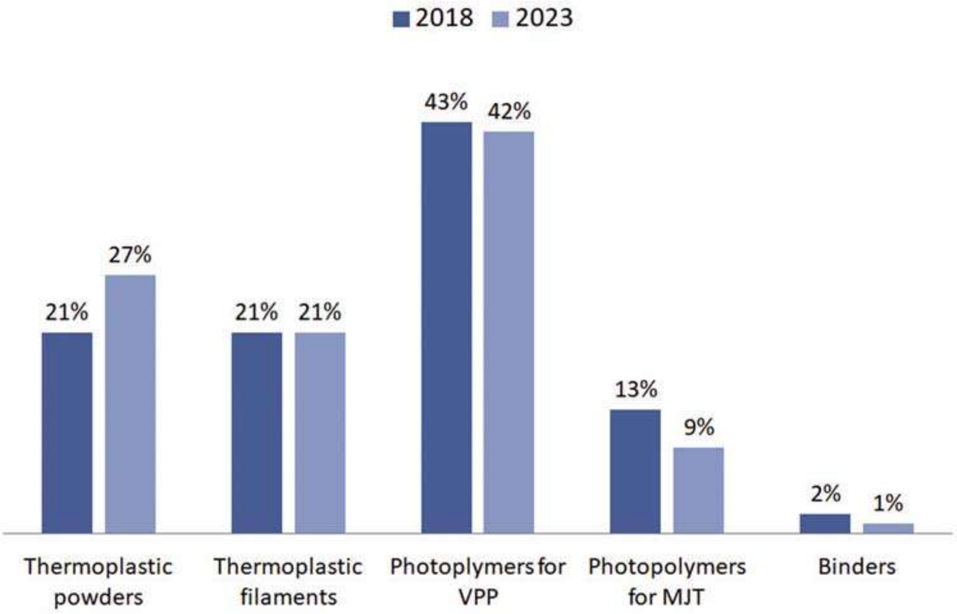

FIGURE 4.1 Use of individual polymer material groups in AM. *(Compiled from Smartech Publishing data [15]).*

4.2 Liquid polymers – photopolymer resins, binders, and viscous ink

Liquid polymers are usually solidified by UV light or by thermal treatment. Based on their properties and use in AM processes, they can be divided into photopolymer resins and binders. The former constitute by far the largest group of polymeric materials used in AM (see Fig. 4.1). Photopolymers are primarily used in vatting (VPP) and jetting (MJP) processes. Their formulations are similar, but they vary in viscosity depending on the technology. Low viscosity (>10 Pa s) photoresins are used in VPP. Because of the deposition of material through the inkjet in MJP, resin viscosity is a critical element. Resins for material jetting typically have viscosities that are significantly different at room and elevated temperatures, and are >50 cP and <15–20 cP, respectively. Photopolymer resins can also be used in one of the material extrusion process technologies, which is ultraviolet-assisted direct ink write (UV-DIW), where the extruded material is then UV-fixed. The resins used in DIW are high viscosity materials. In addition, viscous inks (viscosities >10,000 Pa s) are used in standard DIW processes. In contrast, binders are used in BJT technology [10,16–19].

Photopolymer materials used in AM consist of monomers, oligomers, photoinitiators, and various additives modifying the properties of the photopolymer, including: inhibitors, dyes, antifoaming agents, antioxidants, hardening agents, etc. The photopolymerization reaction, which can be cationic or free radical, proceeds in several steps. Commercial AM resins are mixtures of acrylates, epoxides, and other oligomers. Acrylates are responsible for the reaction rate, while epoxides provide the strength and toughness of the solid [2,10,17,20,21]. Fig. 4.2 shows examples of models made from photopolymer resins.

Based on the method of curing the polymer, photopolymer resins can be divided into:

- UV laser resins – polymerization takes place using a UV laser beam,
- UV DLP resins – the polymerization is made with the use of DLP projector or LCD screen backlit by UV diode,
- Daylight resins – polymerization is done using light with a wavelength of 460 nm [22].

Another classification of resins takes into account its type and application and distinguishes between:

- Standard resins (also known as Firm) – standard photopolymers used to make housings, handles, nuts, toys, illustrative dental and architectural models,
- Flexible resins – photopolymers primarily used for components that are designed to absorb compressive forces,
- Industrial resins (also known as high tensile, hard, high temperature) – photopolymers with increased mechanical and thermal strength used primarily for printing commercial prototypes, engineering models, and automotive parts,
- Castable resins – these photopolymers are used by the jewelry industry to make models for casting jewelry,

FIGURE 4.2 Example models made of resins. *(Photo taken during 3D Printing Days in Kielce September 24, 2020).*

- Modeling resins — these photopolymers, like castable, are used by the jewelry industry and by modelers to make precision models,
- Dental model (Transdent) — these photopolymers are used by dentists and orthodontists to make splints, retainers, and viewing models [22—24].

In VPP processes such as SLA and DLP, obtaining high-quality models requires knowledge of the properties of the photopolymer: its viscosity, critical energy for polymerization, photon penetration depth, and printer specifications: its photon wavelength and power density [25]. The first photopolymers used in VPP processes were mixtures of UV photoinitiators and acrylate monomers. Subsequently, vinyl ether resins were introduced. However, both the former and the latter exhibited significant shrinkage leading to object deformation. Further work on photopolymers led to the introduction of epoxy resins. These cationically polymerized photopolymers have less tendency to warp and curl and less shrinkage than acrylates [10,26].

In DLP technology, (meth)acrylate-based photopolymers are widely used due to the relatively low cost of this material, high penetration depth, and customizable mechanical properties [27]. Epoxy resins and resin blends containing epoxy resins are used in the SLA technology. Cationic epoxy resins can contain a variety of compounds to modify their properties, such as polyglycidyl and nonglycidyl epoxy compounds, epoxy phenol novolac compounds, oxirane-(epoxide), oxetane, tetrahydrofuran, and lactone compounds. Suitable cationic UV-radiated photoinitiators include onium and metallocene salts. Example core materials include polysiloxane, polybutadiene, rubber, or other elastomers, while example reactive shells include compounds with epoxy, oxetane, hydroxyl, vinyl ester, vinyl ether, or acrylate groups, or mixtures of these [2,9,10,28].

Photosensitive thermoset polymers are used in MJP processes. Mainly acrylates, acrylics, epoxies and polylactic acid (PLA), and starch are used [1,29,30].

Photo-curable polymers are not recommended as binders for BJT technology. They can be used in special cases to reduce problems related to the migration of the binder after printing, but it should be taken into account that they can lead to leaving empty spaces in the part and are completely unsuitable for producing dense objects with high strength. Special liquid binders — polymers in solvent or aqueous solution — are used for BJT technology. They can be organic or inorganic. The former are more commonly used, while the latter may be chosen if it is important to leave less impurities in the final part [31—33].

Major binders containing an organic cross-linking agent include butyral resins, polyvinyls, polysiloxanes, polyacrylic acids (PAAs), and acrysoles. These typically decompose thermally during postprocessing and leave little residue. An example of an inorganic solution is silica colloids that react with acid and lower the pH to prevent excessive binder migration. There is also research into using aqueous solutions with agents such as starch, dextran, and maltodextrins as binders and adding nanoparticles to the binder to fill voids between powders and improve sinterability and minimize object shrinkage [31,34].

The binder is crucial for obtaining high-quality parts in BJT technology because the printing resolution depends mainly on the size of the binder droplet sprayed on the powder layer, and this depends on the composition of the binder and its properties. Therefore, the binder must have adequate rheological properties (viscosity and surface tension must be in the ranges of 5—20 Pa.s and 35—40 mJ/N, respectively) and stability, have good wettability and sufficient powder binding forces, and be burnable [5,6,32].

4.3 Polymer powders

Polymer powders are mainly used in Powder Bed Fusion (PBF) processes in Selective Laser Sintering (SLS) and Multi Jet Fusion (MJF) technologies and in Binder Jetting (BJT) processes, or possibly in Powder Melt Extrusion (PME) technology. Examples of models made by SLS technology are shown in Fig. 4.3. The polymers used in powder technologies are primarily semicrystalline thermoplastics, but amorphous thermoplastics, bisegmented thermoplastics, or elastomers can also be used [6].

Powder properties affect the AM process as well as the quality and properties of the parts produced from it. The influence of individual powder properties on the final part quality is a complex issue, as each distinct powder property can affect many features of the manufacturing process, as well as they can affect each other. The basic parameters for determining powder properties by powder manufacturers are: powder flowability (defined by powder distribution), particle size, and flowability specifications.

Powder flowability is crucial for forming a homogeneous powder layer of a certain height during the AM manufacturing step. It increases with decreasing width of the powder size distribution, which is determined only by the dimensions of the individual particles of the bulk solid [35]. The average particle size of powders used in PBF is 25—45 μm, while in BJT it is 20—35 μm, with the smallest particle size being 5 μm and the largest 150 μm or more. The size of the powder, its diameter on the other hand affects the accuracy of the part and the finish and roughness of the surface, the smaller the particle the lower the roughness. Furthermore, the particle size of the powder changes the packing of the powder. Also important for free flow and application to the powder platform

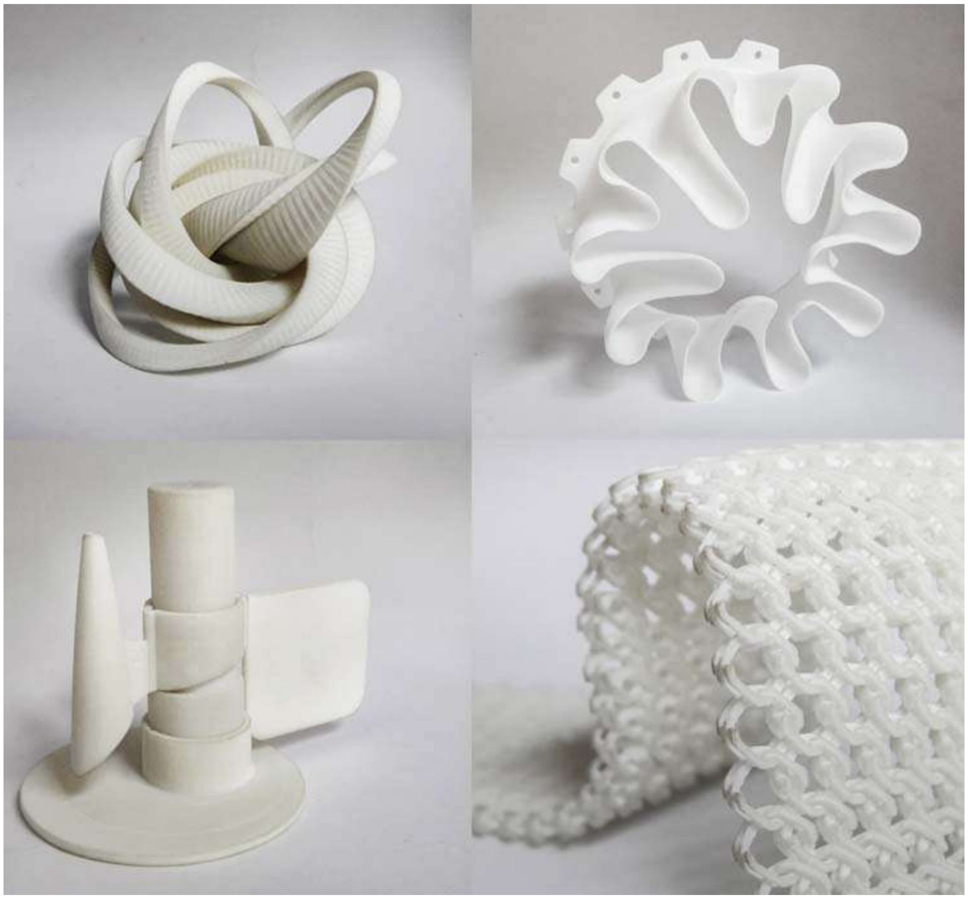

FIGURE 4.3 Examples of models made from powders. *(Photos provided by SYGNIS NEW TECHNOLOGY, https://sygnis.pl/new/en/3d-prints-technologies/).*

are the shape and surface of the individual particles, which should be spherical if possible. In BJT, the height of the overlying powder layer and the packing degree of the powder are very important affecting the strength of the green parts, the lower the height the higher the strength, while the packing degree requires at least 50% packing [29,31,36–42].

The sintering window and sintering stability range of printed polymeric materials are determined by their thermal, rheological, and optical properties. The most important thermal properties include heat capacity, latent heat, transition temperatures, expansion coefficient, thermal decomposition, and thermal conductivity, among others. Rheological properties include, for example, bulk and loss modulus, surface tension, and melt viscosity, while major optical properties include transmission, absorption, and reflection. The deposition rate and layer thickness of polymer powders are determined by flow properties, such as packing factor and avalanche angle, for example [6].

A particularly important issue for materials in powder form is their reusability and recyclability. The recyclability of used polymer powders is related to their molecular properties such as molecular weight, mass distribution, functional groups, molecular bonds, and chemical oxidation. In PBF processes, only a small portion of the powder fed into the machine is used to build parts. Most of the powder remains and can be reused, and there are four methods of using powder from an earlier process, namely:

- the used powder after sieving is mixed with the original powder in a fixed proportion,
- the used powder is mixed with powder of the same age after each cycle,
- the sieved powder is reintroduced after each construction task without mixing with other powders,
- used powder after sieving is added on top of the unused original powder without mixing them [35,42].

Polymer powders are mainly used in SLS and BJT and MJF technologies (see Chapter 3). The choice of powder materials available in the drawing is limited. PBF process mainly uses thermoplastic polymers, with more than 95% of the powder materials being semicrystalline polyamides (PA11 and PA12) [2,38,43–45]. Polyamide 12, as it provides the best performance, poses as much as 90% market share [40,46]. This is due to the relatively good price of these powders and the good repeatability obtained when using them in the AM process. However, PA materials are not suitable for manufacturing corrosion-resistant products and durable surgical implants.

Other powders that can be used in AM processes are: semicrystalline thermoplastics (such as polyamide 6 (PA6), polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polyaryletherketone (PAEK), and polybutylene terephthalate (PBT)); amorphous thermoplastics (e.g., polycarbonate (PC) and polystyrene (PS)); and TPEs (e.g., ester-based polyurethane (TPU)) (see Fig. 4.4) [6,10,38,39,42,43,46,47]. On the other hand, polyglycolic acid (PGA), PLA, polyvinyl alcohol (PVA), poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV), polycaprolactone (PCL), polyethylene oxide (PEO), and their copolymers are applicable in scaffold fabrication and drug delivery devices [2,5,6,28,31].

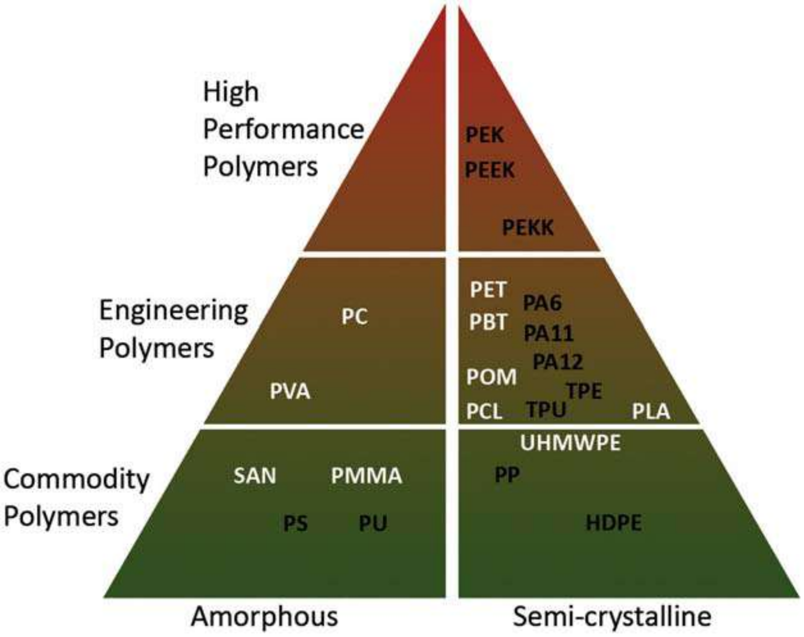

FIGURE 4.4 Polymers used in the form of powders in PBF technologies.

4.4 Filaments and wires

Filament is called a strand of typically 1.75 mm, or 2.85 mm or 3.00 mm in diameter wound on a spool, made from thermoplastic polymers. The filament is made by extruding a molten main polymer combined with fillers, fibers, dyes, and other polymer additives. Filaments are used in MEX processes in Fused Deposition Modeling (FDM) and Fused Filament Fabrication (FFF) technologies, while carbon fiber materials impregnated by thermoplastic polymer matrix in the form of wire or filament is used in DED process.

FDM/FFF is the most common AM technology used for thermoplastic parts (Fig. 4.5). The choice of filaments, made from different types of plastics and composites containing them, is very large. The FDM method can be used to print polymers (Fig. 4.6), polymer matrix composites (PMCs), biocomposites or polymer-ceramic composites

FIGURE 4.5 Example models made of filaments. *(Photo taken during 3D Printing Days in Kielce September 24, 2020).*

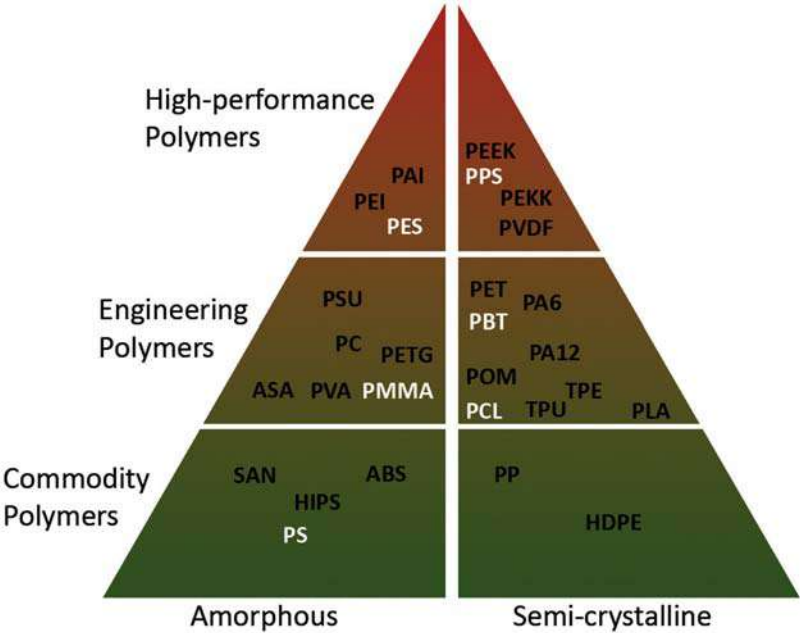

FIGURE 4.6 Thermoplastic polymers used in FDM/FFF technology.

(PCCs), nanocomposites, and fiber-reinforced composites (FRCs). The physical and mechanical properties of the filament and its ease of printing determine the ability to print on a given 3D printer and determine the resulting properties of the printed model. The rheology of the melt, which is influenced by flow rate and temperature, is crucial in determining the printability of new filaments [48–50].

Widely used filament materials include standard and engineered thermoplastics such as: PLA, acrylonitrile-butadiene-styrene (ABS), acrylonitrile-styrene acrylate (ASA), polyethylene terephthalate (PET), glycol-modified polyethylene terephthalate (PETG), nylon (PA), polycarbonate (PC), polypropylene (PP), polyethylene (HDPE), polyvinyl alcohol (PVA), and polycaprolactone (PCL). High-performance polymers, such as polyetheretherketone (PEEK) and polyetherimide (PEI), are also used in 3D printer models where high temperatures can be generated by the print head. In the FDM/FFF technology, with a suitable 3D printer design, flexible polymer materials —TPEs — can also be used. Moreover, limonene-soluble high-impact polystyrene (HIPS) is usually used as a support material. In summary, the largest applications are: ABS, PLA, PC, PET, nylon, ULTEM (polyetherimide), and PEEK or fiber-reinforced thermoplastics [2,5,7,8,28,48,51–57].

The increase in the importance and use of thermoplastic composites in FDM/FFF printing is related to the increase in demand for functional products with nonstandard shapes and the development of printing equipment, such as the use of impregnation in the nozzle, the introduction of a dual print head, or a higher print head temperature. Applications as fillers include carbon nanomaterials, graphene, continuous and short carbon fibers, glass fibers, ceramics, Kevlar, metals (copper, iron fillers, stainless steel, titanium), and biomaterials. ABS, PLA, and nylon are commonly used as matrix materials in fiber-reinforced composites. Most commercialized fiber filaments contain chopped carbon or glass fibers instead of nanofillers. The key is to limit the size of the fillers according to the size of the printing nozzle to avoid clogging [34,48,58,59]. Thermoplastic composites and nanocomposites used as filaments are further discussed in Section 4.7.

Amorphous polymers, such as ABS, PS, PVC, and PMMA, and semicrystalline polymers, such as PP, PE, and PEVA, are used for the production of relatively cheap filaments. Standard resins are used for printing elements operated at low loads. An important group of filaments are materials prepared from engineering polymers, showing moderate temperature resistance and mechanical strength, which include, e.g., PC, PVA (belonging to amorphous polymers), and semicrystalline ones: PLA, PBT, PET, POM, PA, PCL, and PLGA. They are used for printing structural parts. A solution bridging the gap between amorphous and crystalline polymers and eliminating problems with interlayer separation, print quality, or during printing is the use of multimaterial/structure filaments. Blends of ABS with PC, SAN, TPE, PE, SEBS, or PMMA are used as materials, while high-density polyethylene (HDPE) or low-density polyethylene (LDPE) is used as an outer layer. The last group consists of high-performance engineering thermoplastic filaments with very good mechanical, chemical, and thermal properties, which include PEEK, PEK, and PEKK (belonging to PAEK materials), and PVDF, PTFE, PES, PPS, PPSU, PI, and PSU. However, they require high temperatures during 3D printing, which may not be achievable for some FDM printers [34,48,52,53].

The polymers considered easiest to print with and commonly used when printing at home by hobbyists are PLA and PETG. PA and PC are a little more difficult to print with, while ABS requires stable temperature conditions and the use of a chamber to achieve high-quality prints. Nevertheless, the quality of prints made from PET, PC, PA, and ABS is comparable, while the quality from PLA is slightly higher than those mentioned above. Among five commonly used plastics in the form of filaments, ABS and PC show high heat resistance, PET intermediate, while PA and PLA the lowest. The highest elongation at break is characteristic for PA; other materials show similar properties in this aspect. ABS and PC are stronger than other materials — they have better strength properties [48,60].

4.5 Pellets and recycled materials

Resin pellet molds are processed in the extruder into a filament used for FDM/FFF printing; on the other hand, new technologies are being developed such as Fused Granulate Fabrication (FGF) or Fused Pellet Fabrication (FPF), where printing is done directly from pellets. The use of pellets is a cheaper solution than printing from filaments and makes it possible to eliminate the problems brought by the feeding of filament in the FDM/FFF printing process, such as buckling and slippage. The cost of the filament is about 5–10 times higher than the cost of the raw plastic pellets [61]. Besides, direct printing from pellets offers the possibility of easy implementation of new materials such as new multimaterial blends, or the use of materials that are difficult or impossible to form into filament. For the production of filament or direct 3D extrusion printing (FGF/FPF technologies) not only virgin pellets can be used, but also recycled plastic waste as the feedstock. This is an environmentally friendly solution, which is the basis of ongoing research in recent years [62–69].

Generally pellet size ranges from 1 to 3 mm in both diameter and length [51]. However, FPF printers printing from pellets can print a variety of polymeric materials with a wide range of particle sizes and distributions, allowing the printing of a wide range of materials not only in the form of high-quality pellets, but also shredded recycled materials with only minimal postprocessing, i.e., only cleaning and grinding or shredding [63].

The range of polymers in the form of pellets that can be used in 3D printing is analogous to the polymers used in the form of filaments and these are mainly: PLA, ABS, HIPS, PET, and PETG, but printing can also be done from pellets that have restrictions in their use as filaments due to their properties, such as PVDF, PBAT, PCL, or EVA, for example [51,62,63,70–74]. Regarding recyclable and reusable polymers for 3D printing, the polymers investigated include: PLA, HDPE, PP, PET, ABS, elastomers, and composites with wood or carbon fiber. It is worth noting that the selected materials showed suitability for printing even when recycled several times [63–69,74].

4.6 Polymeric sheets and films

Polymer sheets or films have applications in sheet lamination processes. The main material used from the beginning in LOM technology was paper sheets coated with a thermoplastic adhesive [75]. Subsequently, various thermoplastics, including PVC, PMMA, and PC, as well as polymer-based composites, began to be used in LOM [2,76].

The thickness of the film or sheet, which determines the layer thickness of the object produced by LOM technology, is the most influential parameter for final surface roughness. When the layer thickness is higher, the surface is rougher. The standard thickness of paper used in LOM machines is 0.112 mm, but materials with thicknesses of 0.094 mm, 0.100 mm, 0.120 mm, or 0.224 mm are also used [76–80]. In contrast, the thickness of polymeric films is slightly smaller and typically ranges from 0.07 to 0.2 mm [81].

4.7 Polymer composites and nanocomposites

Polymer composites are used to improve the functionality (electrical conductivity, higher thermal conductivity, or biocompatibility) and durability (improved mechanical properties) of polymer printed objects. Composites are materials made by combining two or more monolithic materials, with the stronger, stiffer phase dispersed in a weaker continuous phase (called a matrix). If the dimensions of either phase are on the scale of a billionth of a meter, then the resulting material is classified as a nanocomposite [21,82].

Polymer composites come in the form of filaments, composite or coated powders, and polymers dissolved in an organic solvent. Polymer composites can be processed using such technologies as: inkjet (MJT), FDM/FFF, SLS, DIW, and SLA. Their areas of use are: biomedical applications (bone implants, tissue engineering, scaffolds, drug delivery, etc.), parts with enhanced mechanical properties (fully functioning end use parts, aerospace vehicle, refractory rocket nozzle, bone tissue regeneration and drug delivery, engineering and technology education, applications in engineering disciplines and automotive, frameworks for all-ceramic dental restorations, complex structures, and fabrication of multifunctional materials), parts from materials with enhanced bending/twisting strength (mobile phone, robotics, biocomposites, flexible electronics, memristor, etc.), parts with parts form dielectric materials (flexible and lightweight paper electrode, fabrication of bio diagnostics, artificial insulating material, nano- and microelectromechanical systems, imaging, sensors, electronics, and space-based applications), electrically active parts (smart phones, touch screens, stretchable antenna, light emitting diodes, electronic sensors, capacitive buttons, actuators, conductive microstructures, etc.), parts from materials with controlled thermal properties (heat sink and cooling system, thermoelectric material, rocket motors, thermomechanical materials), with flame-retardant properties, or with enhanced optical properties (luminescent light-converting thin films for AC electroluminescent displays, full color AC-driven displays, electrochromic devices) [75,82–86].

Thermoplastic-based composites are primarily obtained by mixing and extrusion. Composite or coated powders, on the other hand, are prepared by mixing/milling or precipitation by dissolution [5]. Commonly used matrix materials are thermoplastic polymers such as ABS, PLA, or PA. To a lesser extent, PP, PETG, PEEK, or ULTEM is used as matrix (Fig. 4.7). On the other hand, filler components such as fiber-, particle-, or nanoparticle-based materials are used as reinforcement. They can constitute from several to tens of percent of the material. The use of larger amounts of filler in thermoplastic composites is possible in DIW technology and some filaments, where the fiber content can be as high as 40% or more [5,59]. At the same time, fibers have a significant influence on the viscosity of the composite material (they increase it), which affects the process. They also influence the porosity of the 3D printed parts, initially they can even improve it, and with increasing additive proportion they usually worsen it. Reinforcement

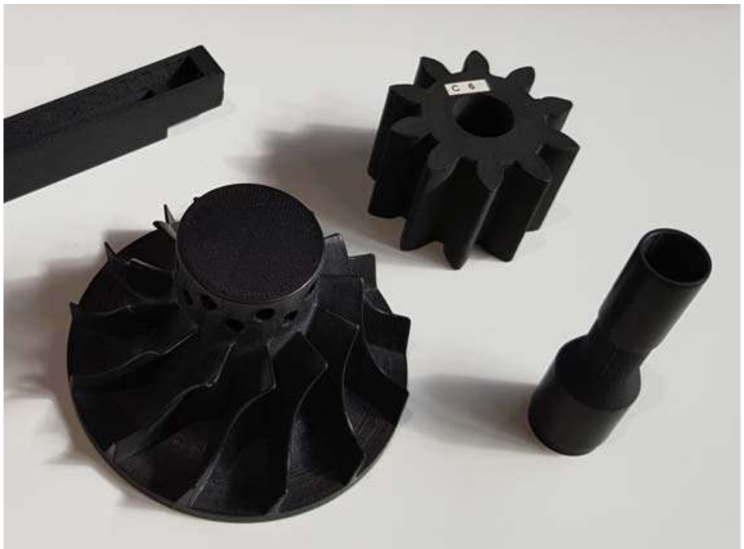

FIGURE 4.7 Example models made of nanocomposite – PEEK with nanotubes. *(Photo taken during the 3D Printing Days in Kielce September 24, 2020).*

fibers can be either continuous or discontinuous (short) fibers. Continuous fibers, despite having a long aspect ratio and preferred orientation, resulting in such composites having higher strength and stiffness, are less commonly used (requiring specialized printing equipment). In contrast, short fibers have a short aspect ratio and usually a random orientation, but are easy to use and economical. Mainly carbon and glass fibers are used as short reinforcing fibers, although recently basalt fibers, or Kevlar, are also growing in importance [6,45,58,84,87–91].

Examples of composites used in various AM technologies are given later in the chapter, and Fig. 4.7 shows models printed using nanomaterial-reinforced composites and FDM technology.

The following thermoplastic composites and nanocomposites are used in FDM/FFF technologies:

- particle-reinforced composites:
  - iron/nylon composites,
  - iron/acrylonitrile butadiene styrene (ABS) composites,
  - copper/acrylonitrile butadiene styrene and iron/acrylonitrile butadiene styrene composites,
  - carbon black/polypropylene/homopolypropylene composite,
  - strontium titanate ($SrTiO_3$)/acrylonitrile butadiene styrene composites,
  - alumina (Al_2O_3)/acrylonitrile butadiene styrene composites,
  - tricalcium phosphate/polypropylene composites,
  - alumina (Al_2O_3)/nylon6 composites,
  - hydroxyapatite/PLA composites,
  - graphite/PA6/PS/POE-g-MAH composites,
- natural fiber–reinforced composites:
  - jute fiber/acrylonitrile butadiene styrene composites,
  - jute fiber/PLA composites,
- synthetic fiber–reinforced composites:
  - carbon fiber/PLA composites,
  - carbon fiber/acrylonitrile butadiene styrene composites,
  - continuous glass, carbon, and kevlar fibers/nylon composites,
  - continuous carbon fiber/PLA composites,
- nanomaterial-reinforced composites:
  - polyurethane/PLA/graphene oxide nanocomposites (TPU/PLA/GO),
  - carbon nanotubes and graphene fillers/polybutylene terephthalate (PBT) composites,
  - zinc oxide nanorod/acrylonitrile butadiene styrene composites,
  - graphene nanoplatelets/acrylonitrile butadiene styrene composites,
  - cloisite/PLA composites,
  - titanium oxide/acrylonitrile butadiene styrene composites,
  - graphene-doped polylactic acid/polylactic acid (G-PLA/PLA),

- polymer blends:
  - ABS/SEBS/UHMWPE polymer blends,
  - UHMWPE/HDPE/PEG polymer blends,
  - PC/SEBS-g-MA polymer blends [5,10,55,59,88,92–94].

Advanced thermoplastic composites and nanocomposites used in SLS include:

- particle-reinforced composites:
  - hydroxyapatite-reinforced polyethylene/polyamide composites (HA-PE/PA),
  - carbon black/polyamide 12 (CB/PA12),
- synthetic fiber–reinforced composites—carbon fiber/polyamide 12 composites,
- nanomaterial-reinforced composites:
  - nanosilica/polyamide 12 composites,
  - nanosilica/polyamide 11 composites,
  - nanoclay/polyamide 6 composites,
  - functionalized graphite nanoplatelets/polyamide 12 composites,
  - carbon nanotube/polyamide 12 composites [5,10,95].

The relatively newest advanced thermoplastic composites and nanocomposites are used in DIW, where the following can be listed:

- nanomaterial-reinforced composites:
  - carbon nanotubes/polylactic acid composites (CNT/PLA),
  - multiwalled carbon nanotube/polylactic acid composites (MWCNT/PLA) [5].

Examples of composites studied for SLA technology include:

- particle-reinforced composites:
  - yttria stabilized zirconia and acrylate and methacrylate (thermoplastics) composites,
  - bioglass and acrylate resin (thermoset) composites,
  - SiOC and SiC and polyramic (SPR-212) (thermoset) composites,
  - boron nitride and methacrylate oligomers (thermoset) composites,
  - urea, resorcinol, and ammonium chloride and PMMA (thermoplastic) composites,
- nanomaterial-reinforced composites:
  - PEGDA and copper nanoparticle–reinforced beams composites,
  - magnetite nanoparticles/PEGDA composites (MNPs/PEGDA),
  - graphen/PEGDA composites,
  - graphen/Envision-TEC composites [21,96].

4.8 Biopolymers, hydrogels, and smart materials

Biopolymers and hydrogels have applications in biomedical 3D printing. The biomedical market has a significant impact on the development of AM technologies and new materials, and it represents a significant portion of the AM market [3]. The main application area of AM technology is bioprinting scaffolds and tissue engineering, although research is underway to produce in the future artificial organs (e.g., bionic ear) or to repair organs and tissues in situ [3,54].

The technique commonly used to print scaffolds is SLA, although bone scaffolds are also often created using FDM. In addition, DLP, SLS, or DIW technologies are also used in biomedical 3D printing. The main polymers used in 3D printing of biomaterials are polyethylene glycol diacrylate (PEGDA), PLA, and polycaprolactone (PCL). These polymers are not photosensitive and therefore require functionalization with methacrylate, diacrylate, or fumarate groups to obtain a photopolymer resin [29]. PEGDA has applications for hydrogel production in scaffold printing. Hydrogels are polymers dispersed in an aqueous environment. SLA, DLP, and DIW technologies are used to print them [19,97]. In 3D bone scaffolds printing, polymeric materials containing hydroxyapatite and various polymers such as poly(ester urea), poly(propylene fumarate) or PCL, and PLA are used. Other materials that have been investigated and used for printing scaffolds are: cellulose (cellulose-starch and cellulose acetate thermoplastic materials), HIPS filament, poly(tri(ethylene glycol)adipate) dimethacrylate (PTEGA-DMA), hydroxyapatite mixed with PLA, polyester PPF, polyesters (poly(hydroxyalkanoate) (PHA)), biodegradable PU elastic nanoparticles with hyaluronan and bioactive ingredients (TGFβ3), copolymers of trimethylene carbonate and poly(ε-caprolactone), photo-cross-linkable poly(propylene fumarate), biodegradable poly(D,L-lactide) macromonomers functionalized with methacrylate end groups, modified diblock copolymers, sodium alginate, chitosan and acrylates-based polymers, composites of HA/PVA [21,28,54,75,98]. Other examples of polymers in biomedical applications include: manufacturing of hip and knee implants using SLS technology and ultrahigh-molecular-weight polyethylene (UHMWPE) material, polymeric stents using FDM technology with thermoplastic polyester elastomer (FlexiFil), or orthopedic screws with PGA and PLA, as well as components for craniofacial reconstruction in patients from an antibacterial composite based on bioactive glass (BAG) and PMMA [28].

Smart materials are used together with smart design in 4D printing. Smart materials are polymers, hydrogels, ceramics, metals, and alloys that have the ability to expand, bend, and deform in response to a specific stimulus, such as a change in temperature (thermoreactive materials), light (photoreactive materials), moisture (chemoreactive materials), a solvent, a change in pH, electricity (electroreactive materials), stress/pressure (mechanoreactive materials), or a magnetic field (magnetoreactive materials). Smart polymers are the most important in 4D printing, while most available materials are heat reactive [2,28,54,99–101].

Smart materials have applications in biomedicine, robotics, and industry. They are an important element of technological innovation in AM, with research encompassing both work on new materials and device modifications for which multiple materials are repeatedly desired. Most commonly, the use of multiple materials provides a better strain, larger angles of actuation, faster shape recovery, better shape fixity, and higher possible complexity of the design. For 4D printing of smart materials, due to the simplicity of the equipment and its low cost, FDM technology is primarily applicable, but PolyJet, DLP, DIW, and SLA are also successfully used [102,103].

Shape memory polymers (SMPs) are an example of smart materials [85]. Shape memory materials (SMP) can respond to one or several stimuli (multistimulus materials). Shape memory effect (SME) is categorized into three sections: one-way SME, two-way SME that is reversible, and the control of SME actuation of recent years with a high degree of freedom. The simplest SME is achieved in a one-way actuation of SMPs. Most SMPs used in 4D printing are amorphous SMPs that react to heat. Semicrystalline SMPs differ from amorphous SMPs by a transition in which the state of the material changes rapidly as the structure reaches a certain temperature. Popular SMPs are polymers based on polyurethane (PU) and PLA. Hydrogels, on the other hand, are widely used in bidirectional activation. In control of SME, composites made of SMP and other materials are applicable [102]. Examples of smart materials include: PCL macromethacrylate, PLA/Fe_3O_4 composite, PLA and poly(ethylene glycol) (PEG) composites, composite of PLA infused with CNT, PLA and thermochromic pigments, graphene polylactic acid (GPLA), UV-curable thermochromic SMP liquid resin, acrylate-based photosensitive resins, composite of polyurethane having DA bonds and carbon nanotubes, and composite of TPU infused with CNTs [28,102,104].

4.9 Conclusions

The type of material and its properties influence the choice of AM technology and determine the quality of the final part. Polymers are the key material for AM processes (Table 4.1). Their use has been dominant for many years

TABLE 4.1 Polymer material categories for specific AM processes.

	Liquid polymers					
AM process	**Photopolymer resins**	**Binders**	**Polymeric powders**	**Pellets**	**Filaments/wires**	**Polymeric sheets/films**
Binder jetting		x	x			
Directed energy deposition					x	
Material extrusion				x	x	
Material jetting	x					
Powder bed fusion			x			
Sheet lamination						x
Vat photopolymerization	x					

and will continue to be so. What is more, new research directions leading to the implementation of new materials and a better understanding of the relations between their properties and process parameters make the application of AM technology more and more extensive. Additionally, the increasing use of polymer composites further widens the scope of AM technology application possibilities and obtaining specific functionalities of manufactured parts.

References

[1] I. Jasiuk, D.W. Abueidda, C. Kozuch, S. Pang, F.Y. Su, J. Mckittrick, An overview on additive manufacturing of polymers, J. Occup. Med. 70 (3) (2018) 275–283.

[2] S.C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, Polymers for 3D printing and customized additive manufacturing, Chem. Rev. 117 (2017) 10212–10290.

[3] T.D. Ngo, A. Kashani, G. Imbalzano, K.T.Q. Nguyen, D. Hui, Additive manufacturing (3D printing): a review of materials, methods, applications and challenges, Compos. B 143 (2018) 172–196, https://doi.org/10.1016/j.compositesb.2018.02.012.

[4] S.S. Alghamdi, S. John, N.R. Choudhury, N.K. Dutta, Additive manufacturing of polymer materials: progress, promise and challenges, Polymers 13 (5) (2021) 753, https://doi.org/10.3390/polym13050753.

[5] A.D. Valino, J.R.C. Dizon, A.H. Espera, Q. Chen, J. Messman, R.C. Advincula, Advances in 3D printing of thermoplastic polymer composites and nanocomposites, Prog. Polym. Sci. 98 (2019) 101162, https://doi.org/10.1016/j.progpolymsci.2019.101162.

[6] S. Yuan, F. Shen, C.K. Chua, K. Zhou, Polymeric composites for powder-based additive manufacturing: materials and applications, Prog. Polym. Sci. 91 (2019) 141–168, https://doi.org/10.1016/j.progpolymsci.2018.11.001.

[7] H. Lee, R. Eom, Y. Lee, Evaluation of the mechanical properties of porous thermoplastic polyurethane obtained by 3D printing for protective gear, Adv. Mater. Sci. Eng. 2019 (2019) 10, https://doi.org/10.1155/2019/5838361.

[8] A. Saxena, A comprehensive study on 3D printing technology, MIT Int. J. Mech. Eng. 6 (2) (2016) 63–69.

[9] J. Herzberger, J.M. Sirrine, C.B. Williams, T.E. Long, Polymer design for 3D printing elastomers: recent advances in structure, properties, and printing, Prog. Polym. Sci. 97 (2019) 101144, https://doi.org/10.1016/j.progpolymsci.2019.101144.

[10] D. Bourell, J.P. Kruth, M. Leu, G. Levy, D. Rosen, A.M. Beese, A. Clare, Materials for additive manufacturing, CIRP Ann. 66 (2) (2017) 659–681, https://doi.org/10.1016/j.cirp.2017.05.009.

[11] Jabil, 3D Printing Trends: Six Major Developments, 2021, https://www.jabil.com/blog/3d-printing-trends-show-positive-outlook.html (Accessed 19 July 2021).

[12] Statista, Leading 3D Printing Materials From 2020, 2020, https://www.statista.com/statistics/560323/worldwide-survey-3d-printing-top-technologies/ (Accessed 19 July 2021).

[13] R. Grace, A look at the Shifting Trends in Additive Manufacturing (k-online.com), 2021, https://mag.k-online.com/en/Menue/Panorama/A_look_at_the_shifting_trends_in_additive_manufacturing (Accessed 19 July 2021).

[14] T. Caffrey, T. Wohlers, R.I. Campbell, Executive Summary of the Wohlers Report 2016, Wohlers, Fort Collins, CO, 2019.

[15] Smartech Markets Publishing & 3dpbm, Additive Manufacturing Opportunities in 2018–2023, 2018, https://www.smartechanalysis.com/wp-content/uploads/2018/11/3dpbm-x-smartech-am-opportunities-in-polymers.pdf (Accessed 19 July 2021).

[16] D.A. Rau, M. Forgiarini, C.B. Williams, Hybridizing direct ink write and mask-projection vat photopolymerization to enable additive manufacturing of high viscosity photopolymer resins, Addit. Manuf. 42 (2021) 101996, https://doi.org/10.1016/j.addma.2021.101996.

[17] A. Navaruckiene, E. Skliutas, S. Kasetaite, S. Rekštytė, V. Raudoniene, D. Bridziuviene, M. Malinauskas, J. Ostrauskaite, Vanillin acrylate-based resins for optical 3D printing, Polymers 12 (2020) 397, https://doi.org/10.3390/polym12020397.

[18] Z. Jiao, F. Li, L. Xie, X. Liu, B. Chi, W. Yang, Experimental research of drop-on-demand droplet jetting 3D printing with molten polymer, J. Appl. Polym. Sci. 135 (9) (2018) 45933, https://doi.org/10.1002/app.45933.

[19] M. Layani, X. Wang, S. Magdassi, Novel materials for 3D printing by photopolymerization, Adv. Mater. 30 (2018) 1706344, https://doi.org/10.1002/adma.201706344.

[20] J.V. Crivello, E. Reichmanis, Photopolymer materials and processes for advanced technologies, Chem. Mater. 26 (2014) 533–548.

[21] J.Z. Manapat, Q. Chen, P. Ye, R.C. Advincula, 3D printing of polymer nanocomposites via stereolithography, Macromol. Mater. Eng. 302 (2017) 1600553, https://doi.org/10.1002/mame.201600553.

[22] Ł. Długosz, Przegląd dostepnych rodzajów żywic w niskobudżetowym druku 3D z fotopolimerów (Overview of Available Resin Types in Low-Budget Photopolymer 3D Printing), 2018, https://centrumdruku3d.pl/przeglad-dostepnych-rodzajow-zywic-w-niskobudzetowym-druku-3d-z-fotopolimerow/ (Accessed 10 July 2018).

[23] L. Vassos, How to Design Parts for Material Jetting 3D Printing, https://www.hubs.com/knowledge-base/how-design-parts-material-jetting-3d-printing/ (Accessed 10 July 2021).

[24] C. Armstrong, How to Design Parts for SLA 3D Printing, https://www.hubs.com/knowledge-base/how-design-parts-sla-3d-printing/ (Accessed 10 July 2021).

[25] I. Gibson, D. Rosen, B. Stucker, Additive Manufacturing Technologies, Springer, New York, NY, 2015, https://doi.org/10.1007/978-1-4939-2113-3_7.

[26] X. Kuang, Z. Zhao, K. Chen, D. Fang, G. Kang, H.J. Qi, High-speed 3D printing of high-performance thermosetting polymers via two-stage curing, Macromol. Rapid Commun. 39 (2018) 1700809, https://doi.org/10.1002/marc.201700809.

[27] K. Kowsari, B. Zhang, S. Panjwani, Z. Chen, H. Hingorani, S. Akbari, N.X. Fang, Q. Ge, Photopolymer formulation to minimize feature size, surface roughness, and stair-stepping in digital light processing-based three-dimensional printing, Addit. Manuf. 24 (2018) 627–638, https://doi.org/10.1016/j.addma.2018.10.037.

[28] C.M. González-Henríquez, M.A. Sarabia-Vallejos, J. Rodriguez-Hernandez, Polymers for additive manufacturing and 4D-printing: materials, methodologies, and biomedical applications, Prog. Polym. Sci. 94 (2019) 57–116, https://doi.org/10.1016/j.progpolymsci.2019.03.001.

[29] M. Van den Eynde, P. Van Puyvelde, 3D printing of poly(lactic acid), Adv. Polym. Sci. 282 (2018) 139–158, https://doi.org/10.1007/12_2017_28.

[30] C. Kundera, T. Kozior, Evaluation of the rheological properties of photopolymers used in polymer jetting technology, MATEC Web Conf. 254 (2019) 07001, https://doi.org/10.1051/matecconf/201925407001.

[31] M. Ziaee, N.B. Crane, Binder jetting: a review of process, materials, and methods, Addit. Manuf. 28 (2019) 781–801, https://doi.org/10.1016/j.addma.2019.05.031.

[32] A. Mostafaei, A.M. Elliott, J.E. Barnes, F. Li, W. Tan, C.L. Cramer, P. Nandwana, M. Chmielus, Binder jet 3D printing—process parameters, materials, properties, modeling, and challenges, Prog. Mater. Sci. 119 (2021) 100707, https://doi.org/10.1016/j.pmatsci.2020.100707.

[33] Y. Guo, H.S. Patanwala, B. Bognet, A.W.K. Ma, Inkjet and inkjet-based 3D printing: connecting fluid properties and printing performance, Rapid Prototyp. J. 23 (3) (2017) 562–576, https://doi.org/10.1108/RPJ-05-2016-0076.

[34] W. Xu, S. Jambhulkar, Y. Zhu, D. Ravichandran, M. Kakarla, B. Vernon, D.G. Lott, et al., 3D printing for polymer/particle-based processing: a review, Compos. B Eng. 223 (2021) 109102, https://doi.org/10.1016/j.compositesb.2021.109102.

[35] S. Vock, B. Klöden, A. Kirchner, T. Weißgärber, B. Kieback, Powders for powder bed fusion: a review, Prog. Addit. Manuf. 4 (2019) 383–397.

[36] H. Miyanaji, K.M. Rahman, M. Da, C.B. Williams, Effect of fine powder particles on quality of binder jetting parts, Addit. Manuf. 36 (2020) 101587, https://doi.org/10.1016/j.addma.2020.101587.

[37] F. Dini, S.A. Ghaffari, J. Jafar, R. Hamidreza, S. Marjan, A review of binder jet process parameters; powder, binder, printing and sintering condition, Met. Powder Rep. 75 (2) (2020) 95–100, https://doi.org/10.1016/j.mprp.2019.05.001.

[38] X. Gong, X. Gao, N. Yu, D. Zhang, L. Tan, J. Li, Characterization of thermally treated polypropylene powders with wide sintering window for powder bed fusion of polymers, Polym. Test. 96 (2021) 107078, https://doi.org/10.1016/j.polymertesting.2021.107078.

[39] M. Schmid, K. Wegener, Additive manufacturing: polymers applicable for laser sintering (LS), Proc. Eng. 149 (2016) 457–464.

[40] D. Drummer, M. Medina-Hernández, M. Drexler, K. Wudy, Polymer powder production for laser melting through immiscible blends, Proc. Eng. 102 (2015) 1918–1925, https://doi.org/10.1016/j.proeng.2015.01.332.

[41] C.N. Nwogu, R. Uche, J.O. Igbokwe, A.C. Okoronkwo, Characterization of recycled polyethylene terephthalate powder for 3D printing feedstock, FUOYE J. Eng. Technol. 4 (2) (2019) 144–148.

[42] R.D. Goodridge, C.J. Tuck, R.J.M. Hague, Laser sintering of polyamides and other polymers, Prog. Mater. Sci. 57 (2) (2012) 229–267, https://doi.org/10.1016/j.pmatsci.2011.04.001.

[43] A. Wegner, New polymer materials for the laser sintering process: polypropylene and others, Phys. Proc. 83 (2016) 1003–1012, https://doi.org/10.1016/j.phpro.2016.08.105.

[44] H. Zarringhalam, N. Hopkinson, N.F. Kamperman, J.J. de Vlieger, Effects of processing on microstructure and properties of SLS Nylon 12, Mater. Sci. Eng. 435–436 (2006) 172–180, https://doi.org/10.1016/j.msea.2006.07.084.

[45] H. Miyanaji, J.M. Akbar, L. Yang, Fabrication and characterization of Graphite/Nylon 12 composite via binder jetting additive manufacturing process, in: Conference Paper: 28th Annual International Solid Freeform Fabrication Symposium - an Additive Manufacturing Conference, August 2017.

[46] H. Gu, F. AlFayez, T. Ahmed, Z. Bashir, Poly(ethylene terephthalate) powder—a versatile material for additive manufacturing, Polymers 11 (2019) 2041, https://doi.org/10.3390/polym11122041.

[47] D.L. Bourell, T.J. Watt, D.K. Leigh, B. Fulcher, Performance limitations in polymer laser sintering, Phys. Proc. 56 (2014) 147–156, https://doi.org/10.1016/j.phpro.2014.08.157.

[48] S. Park, K. Fu, Polymer-based filament feedstock for additive manufacturing, Compos. Sci. Technol. 213 (2021) 108876, https://doi.org/10.1016/j.compscitech.2021.108876.

[49] D.A. Porter, T.V.T. Hoang, T.A. Berfield, Effects of in-situ poling and process parameters on fused filament fabrication printed PVDF sheet mechanical and electrical properties, Addit. Manuf. 13 (2017) 81–92, https://doi.org/10.1016/j.addma.2016.11.005.

[50] A. Charles, P.M. Bassan, T. Mueller, A. Elkaseer, S.G. Scholz, Chapter 30. On the assessment of thermo-mechanical degradability of multi-recycled ABS polymer for 3D printing applications, in: P. Ball, et al. (Eds.), Sustainable Design and Manufacturing 2019, Smart Innovation, Systems and Technologies, Springer Nature Singapore Pte Ltd., 2019, https://doi.org/10.1007/978-981-13-9271-9_30.

[51] S. Whyman, K.M. Arif, J. Potgieter, Design and development of an extrusion system for 3D printing biopolymer pellets, Int. J. Adv. Manuf. Technol. 96 (2018) 3417–3428.

[52] S. Garzon-Hernandez, A. Arias, D. Garcia-Gonzalez, A continuum constitutive model for FDM 3D printed thermoplastics, Compos. B Eng. 201 (2020) 108373, https://doi.org/10.1016/j.compositesb.2020.108373.

[53] S. Wojtyła, P. Klama, T. Baran, Is 3D printing safe? Analysis of the thermal treatment of thermoplastics: ABS, PLA, PET, and nylon, J. Occup. Environ. Hyg. 14 (6) (2017) D80–D85, https://doi.org/10.1080/15459624.2017.1285489.

[54] J.-Y. Lee, J. An, C.K. Chua, Fundamentals and applications of 3D printing for novel materials, Appl. Mater. Today 7 (2017) 120–133.

[55] A. Przybytek, J. Kucińska-Lipka, H. Janik, Thermoplastic elastomer filaments and their application in 3D printing, Elastomery 4 (20) (2016) 32–39.

[56] T.N.A.T. Rahim, A.M. Abdullah, H.M. Akil, Recent developments in fused deposition modeling-based 3D printing of polymers and their composites, Polym. Rev. 59 (4) (2019) 589–624, https://doi.org/10.1080/15583724.2019.1597883.

[57] H. Wu, W.P. Fahy, S. Kim, H. Kim, N. Zhao, L. Pilato, A. Kafi, S. Bateman, J.H. Koo, Recent developments in polymers/polymer nanocomposites for additive manufacturing, Prog. Mater. Sci. 111 (2020) 100638, https://doi.org/10.1016/j.pmatsci.2020.100638.

[58] S. Wickramasinghe, T. Do, P. Tran, FDM-based 3D printing of polymer and associated composite: a review on mechanical properties, defects and treatments, Polymers 12 (2020) 1529, https://doi.org/10.3390/polym12071529.

[59] T. Mulholland, S. Goris, J. Boxleitner, T.A. Osswald, N. Rudolph, Process-induced fiber orientation in fused filament fabrication, J. Compos. Sci. 2 (3) (2018) 45, https://doi.org/10.3390/jcs2030045.

[60] T.I. Zohdi, Introduction: additive/3D printing materials—filaments, functionalized inks, and powders, in: Modeling and Simulation of Functionalized Materials for Additive Manufacturing and 3D Printing: Continuous and Discrete Media, Lecture Notes in Applied and Computational Mechanics, vol. 60, Springer, Cham, 2018, https://doi.org/10.1007/978-3-319-70079-3_1.

[61] A.L. Woern, J.M. Pearce, 3-D printable polymer pelletizer chopper for fused granular fabrication-based additive manufacturing, Inventions 3 (78) (2018) 1–17, https://doi.org/10.3390/inventions3040078.

[62] J. Lehrer, M.R. Scanlon, The Development of a Sustainable Technology for 3D Printing Using Recycled Materials, Paper presented at 2017 Mid-Atlantic Section Fall Conference, Penn State University - Berks Campus - Reading, Pennsylvania, October 2017, https://peer.asee.org/29391.

[63] A.L. Woern, D.J. Byard, R.B. Oakley, M.J. Fiedler, S.L. Snabes, J.M. Pearce, Fused particle fabrication 3-D printing: recycled materials' optimization and mechanical properties, Materials 11 (2018) 1413, https://doi.org/10.3390/ma11081413.

[64] F.A.C. Sanchez, H. Boudaoud, S. Hoppe, M. Camargo, Polymer recycling in an open-source additive manufacturing context: mechanical issues, Addit. Manuf. 17 (2017) 87–105, https://doi.org/10.1016/j.addma.2017.05.013.

[65] I. Anderson, Mechanical properties of specimens 3D printed with virgin and recycled polylactic acid, 3D Print. Addit. Manuf. 4 (2017) 110–115.

[66] S. Chong, G.-T. Pan, M. Khalid, T.C.-K. Yang, S.-T. Hung, C.-M. Huang, Physical characterization and pre-assessment of recycled high-density polyethylene as 3D printing material, J. Polym. Environ. 25 (2017) 136–145, https://doi.org/10.1007/s10924-016-0793-4.

[67] M.I. Mohammed, A. Das, E. Gomez-Kervin, D. Wilson, I. Gibson, EcoPrinting: investigating the use of 100% recycled acrylonitrile butadiene styrene (ABS) for additive manufacturing. Solid freeform fabrication 2017, in: Proceedings of the 28th Annual International Solid Freeform Fabrication Symposium, 7-9 August 2017. Austin, TX, USA.

[68] N. Volpato, D. Kretschek, J.A. Foggiatto, C.M. Gomez da Silva Cruz, Experimental analysis of an extrusion system for additive manufacturing based on polymer pellets, Int. J. Adv. Manuf. Technol. 81 (2015) 1519–1531, https://doi.org/10.1007/s00170-015-7300-2.

[69] S. Singamneni, D. Smith, M.-J. LeGuen, D. Truong, Extrusion 3D printing of polybutyrate-adipate-terephthalate-polymer composites in the pellet form, Polymers 10 (2018) 922, https://doi.org/10.3390/polym10080922.

[70] N. Momenzadeh, H. Miyanaji, D.A. Porter, T.A. Berfield, Polyvinylidene fluoride (PVDF) as a feedstock for material extrusion additive manufacturing, Rapid Prototyp. J. 1 (26) (2020) 156–163, https://doi.org/10.1108/RPJ-08-2018-0203.

[71] S. Liu, P. Zhao, S. Wu, C. Zhang, J. Fu, Z. Chen, A pellet 3D printer: device design and process parameters optimization, Adv. Polym. Technol. 2019 (2019) 8, https://doi.org/10.1155/2019/5075327.

[72] C. Lee, J.A. Tarbutton, Polyvinylidene fluoride (PVDF) direct printing for sensors and actuators, Int. J. Adv. Manuf. Technol. 104 (2019) 3155–3162, https://doi.org/10.1007/s00170-019-04275-z.

[73] N. Kumar, P.K. Jain, P. Tandon, P.M. Pandey, The effect of process parameters on tensile behavior of 3D printed flexible parts of ethylene vinyl acetate (EVA), J. Manuf. Process. 35 (2018) 317–326, https://doi.org/10.1016/j.jmapro.2018.08.013.

[74] P. Surve, P. Gopathi, Possibilities and Limitations of Using Production Waste PET and PES Materials in Additive Manufacturing (3D Printing Technology), Master Thesis, Halmstad University, Halmstad, 2017.

[75] Q. Wang, J. Sun, Q. Yao, C. Ji, J. Liu, Q. Zhu, 3D printing with cellulose materials, Cellulose 25 (2018) 4275–4301, https://doi.org/10.1007/s10570-018-1888-y.

[76] D. Olivier, J.A. Travieso-Rodriguez, S. Borros, G. Reyes, R. Jerez-Mesa, Influence of building orientation on the flexural strength of laminated object manufacturing specimens, J. Mech. Sci. Technol. 31 (2017) 133–139, https://doi.org/10.1007/s12206-016-1212-4.

[77] D. Ahn, J.-H. Kweon, J. Choi, S. Lee, Quantification of surface roughness of parts processed by laminated object manufacturing, J. Mater. Process. Technol. 212 (2) (2012) 339–346, https://doi.org/10.1016/j.jmatprotec.2011.08.013.

[78] B.K. Paul, V. Voorakarnam, Effect of layer thickness and orientation angle on surface roughness in laminated object manufacturing, J. Manuf. Process. 3 (2) (2001) 94–101.

[79] A.K. Sridharan, S. Joshi, An octree-based algorithm for the optimization of extraneous material removal in laminated object manufacturing (LOM), J. Manuf. Syst. 19 (6) (2001) 355–364, https://doi.org/10.1016/S0278-6125(01)80007-8.

[80] Y.S. Liao, L.C. Chiu, Y.Y. Chiu, A new approach of online waste removal process for laminated object manufacturing (LOM), J. Mater. Process. Technol. 140 (1–3) (2003) 136–140, https://doi.org/10.1016/S0924-0136(03)00690-3.

[81] A. Pilipović, P. Raos, M. Šercer, Experimental testing of quality of polymer parts produced by laminated object manufacturing – LOM, Tech. Gaz. 18 (2011) 253–260.

[82] S.H.R. Sanei, D. Popescu, 3D-printed carbon fiber reinforced polymer composites: a systematic review, J. Compos. Sci. 4 (98) (2020) 1–23.

[83] U. Kalsoom, P.N. Nesterenko, B. Paull, Recent developments in 3D printable composite materials, RSC Adv. 6 (2016) 60355–60371.

[84] M. Abshirini, M. Charara, P. Marashizadeh, M.C. Saha, M.C. Altan, Y. Liu, Functional nanocomposites for 3D printing of stretchable and wearable sensors, Appl. Nanosci. 9 (2019) 2071–2083, https://doi.org/10.1007/s13204-019-01032-2.

[85] N. Shahrubudin, T. Lee, R. Ramlan, An overview on 3D printing technology: technological, materials, and applications, Proc. Manuf. 35 (2019) 1286–1296, https://doi.org/10.1016/j.promfg.2019.06.089.

[86] H. Vahabi, F. Laoutid, M. Mehrpouya, M.R. Saeb, P. Dubois, Flame retardant polymer materials: an update and the future for 3D printing developments, Mater. Sci. Eng. R Rep. 144 (2021) 100604, https://doi.org/10.1016/j.mser.2020.100604.

[87] L.G. Blok, M.L. Longana, H. Yu, B.K.S. Woods, An investigation into 3D printing of fibre reinforced thermoplastic composites, Addit. Manuf. 22 (2018) 176–186, https://doi.org/10.1016/j.addma.2018.04.039.

[88] A.N. Dickson, H.M. Abourayana, D.P. Dowling, 3D printing of fibre-reinforced thermoplastic composites using fused filament fabrication—a review, Polymers 12 (2020) 2188, https://doi.org/10.3390/polym12102188.

[89] J. Saroia, Y. Wang, Q. Wei, M. Lei, X. Li, Y. Guo, K. Zhang, A review on 3D printed matrix polymer composites: its potential and future challenges, Int. J. Adv. Manuf. Technol. 106 (2020) 1695–1721.

[90] I. Blanco, The use of composite materials in 3D printing, J. Compos. Sci. 4 (2) (2020) 42, https://doi.org/10.3390/jcs4020042.

[91] H. Long, Z. Wu, Q. Dong, Y. Shen, W. Zhou, Y. Luo, C. Zhang, X. Dong, Mechanical and thermal properties of Bamboo fiber reinforced polypropylene/polylactic acid composites for 3D printing, Polym. Eng. Sci. 59 (S2) (2019) E247–E260, https://doi.org/10.1002/pen.25043.

[92] N. Rudolph, T. Mulholland, A. Falke, Filled thermoconductive plastics for fused filament fabrication, in: Conference: Solid Freeform Fabrication 2016, Austin, TX, August 2016.

[93] S. Fafenrot, N. Grimmelsmann, M. Wortmann, A. Ehrmann, Three-dimensional (3D) printing of polymer-metal hybrid materials by fused deposition modeling, Materials 10 (2017) 1199, https://doi.org/10.3390/ma10101199.

[94] F. Alkadi, J. Lee, J.-S. Yeo, S.-H. Hwang, J.-W. Choi, 3D printing of ground tire rubber composites, Int. J. Prec. Eng. Manuf. Green Technol. 6 (2019) 211–222, https://doi.org/10.1007/s40684-019-00023-6.

[95] T. Hupfeld, T. Laumer, T. Stichel, T. Schuffenhauer, J. Heberle, M. Schmidt, S. Barcikowski, B. Gökce, A new approach to coat PA12 powders with laser-generated nanoparticles for selective laser sintering, Proc. CIRP 74 (2018) 244–248, https://doi.org/10.1016/j.procir.2018.08.103.

[96] S. Singh, S. Ramakrishna, F. Berto, 3D printing of polymer composites: a short review, Mat. Design. Process. Comm. 2 (2020) e97, https://doi.org/10.1002/mdp2.97.

[97] D. Chimene, K.K. Lennox, R.R. Kaunas, A.K. Gaharwar, Advanced Bioinks for 3D printing: a materials science perspective, Ann. Biomed. Eng. 44 (2016) 2090–2102, https://doi.org/10.1007/s10439-016-1638-y.

[98] V.S.D. Voet, T. Strating, G.H.M. Schnelting, P. Dijkstra, M. Tietema, J. Xu, A.J.J. Woortman, K. Loos, J. Jager, R. Folkersma, Biobased acrylate photocurable resin formulation for stereolithography 3D printing, ACS Omega 3 (2018) 1403–1408, https://doi.org/10.1021/acsomega.7b01648.

[99] A. Subash, B. Kandasubramanian, 4D printing of shape memory polymers, Eur. Polym. J. 134 (2020) 109771, https://doi.org/10.1016/j.eurpolymj.2020.109771.

[100] M. Falahati, P. Ahmadvand, S. Safaee, Y.-C. Chang, Z. Lyu, R. Chen, L. Li, Y. Lin, Smart polymers and nanocomposites for 3D and 4D printing, Mater. Today 40 (2020) 215–245, https://doi.org/10.1016/j.mattod.2020.06.001.

[101] Z.X. Khoo, J.E.M. Teoh, Y. Liu, C.K. Chua, S. Yang, J. An, K.F. Leong, W.Y. Yeong, 3D printing of smart materials: a review on recent progresses in 4D printing, Virt. Phys. Prototyp. 10 (3) (2015) 103–122, https://doi.org/10.1080/17452759.2015.1097054.

[102] Y.S. Alshebly, M. Nafea, M.S.M. Ali, H.A.F. Almurib, Review on recent advances in 4D printing of shape memory polymers, Eur. Polym. J. 159 (2021) 110708, https://doi.org/10.1016/j.eurpolymj.2021.110708.

[103] X. Wan, L. Luo, Y. Liu, J. Leng, Direct ink writing based 4D printing of materials and their applications, Adv. Sci. 7 (2020) 16, https://doi.org/10.1002/advs.202001000.

[104] X. Li, R. Yu, Y. He, Y. Zhang, X. Yang, X. Zhao, W. Huang, Four-dimensional printing of shape memory polyurethanes with high strength and recyclability based on Diels-Alder chemistry, Polymer 200 (2020) 122532, https://doi.org/10.1016/j.polymer.2020.122532.

CHAPTER

5

Application of 3D printing

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5.1 Introduction

Initially, additive manufacturing (AM) (3D printing) was used primarily by designers for rapid prototyping. The resulting models were aesthetically pleasing and functional, and the time to produce them compared to traditional manufacturing methods used in the product development process was significantly shorter, with a lower total cost incurred. This was made possible by the fact that AM processes can be used to produce single customized units or small quantities of products at relatively low cost.

With the rapid rise in popularity of 3D printing after 2009 and the rapid development of new technologies and materials in the following years, the range of applications of AM in various industries began to change and expand, although significant changes have only occurred in recent years [1,2]. With the ability to produce complex geometries with high precision and repeatability, maximum material savings, flexibility in design, and individual customization, AM is no longer limited to prototyping, but extends to making products on a small but even medium scale. According to data presented in a report compiled by HUBS and Jabil [3,4], AM is increasingly used in mass production. Such a trend is also confirmed by data in a report compiled by Sculpteo [5], according to which in 2020 the use of AM in manufacturing accounted for 49%, while mass production was 13%. However, primary applications are still dominant and so proof-of-concept/test models and prototype were 59% and 68%, respectively. The attitude of professional users is also changing, as they are increasingly shifting from investing in their own equipment to using professional online 3D printing platforms. This is due to the multitude of printing materials and systems available and the cost of investing in them [3,4,6].

5.2 Main applications of 3D printing

AM processes have applications in many industries including: automotive, aerospace, rail, defense, marine, medical and dental, electronics, architecture, sports, art and design, textile industry, food industry, research and science, education, jewelery, consumer goods, etc. [3–5,7,8]. The use of AM technologies in biomedicine, construction, or industry has increased in recent years [9]. Moreover, the compound annual growth rate (CAGR) is projected to increase by 18%–32% by 2026 for the medical industry, automotive industry, aerospace industry, and food industry [1]. AM technologies using metals or metal composites are largely used in heavy industry-related industries. Polymers, on the other hand, are mainly used in proof of concept, prototyping, or hobby printing, and in industries such as biomedical and dental, electronics, sports, consumer goods, and some industrial goods.

The share of AM technology usage according to the Sculpteo report [5] is as follows: R&D/research/education – 42%, mechanical/spare parts – 40%, personal interest/hobby – 32%, tooling – 26%, marketing samples – 21%, art/jewelery/fashion – 20%, other – 7%. A similar distribution of usage is presented in a report compiled by HUBS [3].

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5.2.1 AM processes in prototyping

Prototyping, i.e., the production of a functional design for verification, is the original purpose of AM processes and still the main one (see Section 5.1). A prototype can be made at various stages of the development of a new design to verify the 3D computer model, to assess the fit of components or to perform functional tests, as well as to finally validate the whole design. Prototypes can be produced using any of the available AM technologies, with SLS, FDM, SLA, and MJT being the most applicable.

A wide range of materials with different properties available on the market allows to prepare prototypes very close to finished products. Polymers such as PLA, ABS, and PETG are mainly used in prototyping. The mainly used engineering polymers are: PA, TPU, ASA, and PEI. As far as resins are concerned, their share compared to filaments and powders is small and they are both standard and engineering resins [3].

5.2.2 AM processes in aerospace and defense industries

The aerospace and defense industries are areas that require particularly high-quality engineering to produce high-strength structures. By using AM processes, design freedom is increased while reducing component manufacturing costs and availability times. Also important is the ability to reduce part weight, reduce material consumption compared to traditional technologies, and print components anywhere, even in space.

In the aerospace and defense industry, the most popular application of 3D printing is prototyping (72%), followed by repair (44%), R&D (43%), and production parts (39%) [10]. The applications are mainly AM processes using metals (mainly nickel-based alloys or titanium alloys, or special steels), predominantly PBF processes (and especially direct metal laser sintering (DMLS), electron beam melting (EBM), and selective laser melting (SLM) technologies), and DED (with direct metal deposition (DMD) and laser metal deposition (LMD) technologies). However, flame-retardant polymers and polymer composites are also used in selected applications, with SLS technology being the most commonly used. Moreover, high-performance polymers of PAEKs family and their composites as well as other engineering polymers such as PP, PA6, and PA12 and their composites are used as materials [8,11–19].

5.2.3 AM processes in the automotive industry

After aerospace (18.2%) and industrial/business machines (18.8%), automotive is the industry with the highest use of AM processes amounting to 14.8% [7]. They are used to create both conceptual models and accurate functional prototypes and hard-to-find parts, as well as multimaterial parts with specific properties. Their use enables the creation of lighter, safer, and more environmentally friendly cars, while reducing production time and costs. This is possible through the use of available engineering materials and the use of complex cross sections (e.g., honeycomb cells, recesses in parts) [11,19,20]. At the same time, the weight of automotive parts can be reduced by 40%–80% due to their manufacturing using AM technology [21]. The use of AM processes not only affects the production of the parts themselves, but also changes the supply chain and increases the availability of individual components [22,23].

Although metal is the leading material used in automotive AM manufacturing, polymers also have applications (Figs. 5.1 and 5.2). Parts made of polymers can be produced using AM technologies that are standard for these materials, such as: FDM, SLS, and MJF, BJT, or DLS.

5.2.4 AM processes in electronics

AM processes are successfully used for the direct manufacturing of functional electronics such as antennas, capacitors, resistors, inductors, sensors, flexible displays, and solar cells. Electronics are mainly produced using AM technologies such as inkjet printing with metal nanoparticles, e.g., silver, gold, or copper, or with carbon nanotubes with no need for finishing processes [24–28]. Other AM technologies are also investigated and applied in various electronic applications and so, e.g., BJT, FDM, DIW, and SLA can be used in 3D printing for electrochemistry [29]; moreover BJT also could enable fabrication of a variety of RF electronic components including antennas, filters, and feed horns [30], while FDM, SLA, PBF besides MJT can be used in 3D printing of conductive components using CNT composites [25].

A new area of application for AM is its use of conjugated polymers (CPs) in organic electronics. Using CPs and an appropriate AM technique that does not affect the stability of the polymers, it is possible to produce organic light emitting diodes (OLEDs), organic photovoltaics (OPVs), and organic field-effect transistors (OFETs), among others. Three different AM technologies are used here, namely DIW, SLA, and DLP. An example of a conductive polymer is

FIGURE 5.1 3D printed rims and custom seats. *(Photo taken during 3D Printing Days in Kielce September 24, 2020).*

FIGURE 5.2 Examples of automotive parts made using AM technology. *(Photos taken during 3D Printing Days in Kielce September 24, 2020).*

polyaniline (PANI), which can exist in three different oxidation states. It can also be used as a composite, e.g., PANI with dodecylbenzenesulfonic acid (DBSA), PANI within poly(ethylene glycol) diacrylate (PEGda) or gelatin methacrylate (GelMA) gels, or PANI–graphene oxide composite. Other examples of CPs are conductive PPY and PEDOT, used as, e.g.: poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) paste, polypyrrole: poly(ethylene glycol) diacrylate (PPY:PEGda) [31].

5.2.5 AM processes in medicine and dentistry

Medicine and dentistry are among the most important application areas for AM processes, accounting for 11% of the market [7], moreover dynamically developing with further promising growth forecasts. At the same time, a large part of the research on the application of 3D printing in the biomedical area does not have an applied use, but is only in the research and development phase or the beginnings of clinical trials; nevertheless, it is a particularly important area of great interest.

3D printing technologies enable rapid production of medical implants and are changing the way doctors and surgeons plan procedures. Applications of AM processes in pharmaceuticals and biomedicine include applications such as implants, prosthetics, scaffolds, devices, e.g., hearing aids, printed tissues, and organs, drug delivery, surgical guides, and instruments; soft electronic materials for sensing [8,30,32]. Moreover, in the era of COVID-19 pandemic, 3D printing has found application for manufacturing: medical devices, personal protective equipment, personal accessories, testing devices, training and visualization aids, and emergency dwelling [33,34].

VPP processes are used to manufacture bone, scaffold, implant guides, and hearing aids. PBF processes are used to manufacture models that require a lattice, medical devices such as implants, and fixations. MJF technology has been used to create, e.g.: ankle and foot orthoses, hand prostheses, or helmets used in the treatment of malignant tumors of the scalp. FDM/FFF technologies are used to make medical instruments and devices and rapid prototyping exoskeletons. The BJT technology is mainly used for color models especially color coding of anatomy, while MJT processes are used to create medical models. Sheet lamination processes have been used in orthopedic modeling of bone surfaces [35−38].

3D printing and bioprinting (Fig. 5.3) play an important role in many medical fields such as cardiology and cardiac surgery, orthopedic surgery, plastic surgery, vascular surgery, neurosurgery, transplantation, ophthalmology, gastroenterology, maxillofacial surgery, otolaryngology, podiatry, pulmonology, oncology, urology, etc. Thus, for example, in the case of using 3D printing to treat otolaryngological disorders, as part of tissue engineering of the ear, 3D scaffolds are made that reproduce the anatomy of the auricle or structures capable of regenerating auricle cartilage and restoring auditory function to the ear. Also made are a customized 3D printed incus prosthesis, a nose-shaped scaffold, 3D printed biodegradable splints to treat tracheobronchomalacia, a scaffold imitating the size and shape of the patient's nasal septum defect, etc. Materials used in 3D printing for otolaryngology include: polycaprolactone (PCL), polyglycolic acid (PGA) and polylactic acid (PLA) and polylactic-co-glycolic acid (PLGA), hydrogels enriched with stem cells, and growth factors [35,39,40].

As part of ongoing research, AM technologies are also being used to design personalized drugs with a specific mode of release of active ingredients, which would be expected to provide maximum therapeutic benefit to patients. For the production of pharmaceutical products, SLS technology seems to be particularly useful, as it is considered to be the closest to traditional tablet processes compared to other 3D printing technologies. Moreover, it is very efficient, cost-effective, allows materials to be recycled through reuse, and does not require the use of additional substances and solvents. Biodegradable polymers such as polycaprolactone (PCL) and poly-L-lactide (PLLA) or commercial pharmaceutical grade polymers have been investigated in SLS drug production: Eudragit L100-55, Kollicoat IR, or hydroxypropylmethylcellulose (HPMC) [36,41,42]. BJT technology can also be applied in the production of controlled-release drugs. In this case, resorbable polyesters, i.e., polyethylene oxide, and polycaprolactone can be used as base material [30].

FIGURE 5.3 3D bioprinter for human tissue bioprinting. *(Photo taken during 3D Printing Days in Kielce September 24, 2020).*

FIGURE 5.4 3D printed denture. *(Photo taken during 3D Printing Days in Kielce September 24, 2020).*

In dentistry, the application of AM processes relates to areas such as: orthodontics (3D printed digital models, clear custom-made braces), restorative dentistry and endodontics (3D printed tooth model), prosthetic dentistry (3D printed prosthesis/component, denture fabrication (Fig. 5.4), 3D printed custom-made crowns), implant dentistry (3D printed implants and surgical guides and templates), maxillofacial surgery (3D printed models, implants, and prosthesis) [43].

The use of individual AM technologies in dentistry is following:

- SLA: temporary and permanent crowns, temporary bridges, temporary restorations,
- DLP: temporary and permanent crowns, removable dental prosthesis,
- FDM: surgical guides and templates, dental replica models, denture flasks, bites, mouth guards, oral drug delivery device,
- SLS: custom-made dental implants, partial dentures,
- MJT and BJT: temporary crowns, dental replica models [44].

The main polymers used in dentistry are: vinyl polymers (predominantly poly(methyl methacrylate) (PMMA)) − SLA and SLS technologies; styrene polymers (polystyrene (PS) and acrylonitrile-butadiene-styrene (ABS)) − FDM and SLS technologies; polyesters (polycarbonate (PC), polycaprolactone (PCL), and polylactic acid (PLA)) − FDM technology; and shape memory polymers.

5.2.6 AM processes in research and education

3D printing creates new cognitive and educational opportunities by creating realistic models used for research or learning. For example, 3D printed models of, e.g., complex anatomical structures (such as the human heart, tissue connections), compared to textbook illustrations or even digital models, allow students to better understand and learn, thanks to the possibility of physical exploration of the structures and interaction with the object. Also, expensive models traditionally used in teaching can be replaced by cheap, easy to make 3D printed models. Furthermore, microscopic or small objects can be printed to scale in order to facilitate learning without the need for microscopes or other specialized tools. Objects can also be printed to replace real objects during research, such as complex geometries of sponges and corals have been printed to allow the study of fluid flow around these organisms or other physical models of parts like gears, transmissions, test specimens (Fig. 5.5) for self-assembly or endurance testing [23,45,46]. Furthermore, 3D design and 3D printing can be one of the activities implemented in schools, enabling students to develop creativity and design skills [47].

5.2.7 AM processes in architecture and construction

AM processes make it possible to produce a building model quickly and accurately (Fig. 5.6), thus eliminating the labor-intensive and time-consuming production of spatial mock-ups by architectural firms. Here, AM technologies

FIGURE 5.5 3D printed samples for testing the strength of materials.

FIGURE 5.6 3D printed building model. *(Photo taken during 3D Printing Days in Kielce September 24, 2020).*

such as SLS, SLA, MJT (PolyJet), and polymers as materials are most commonly used. However, making a scale model is not the only possible use of 3D printing in architecture; since 2014 the market has been developing toward the production of prefabricated products for house construction, or even 3D printing of entire houses. Attempts to use 3D printing also include other building structures such as a pedestrian bridge [46,48–51].

5.2.8 AM processes in culture and the arts, industrial design, jewelery, and fashion industries

AM processes in industrial design, art, and fashion enable concept validation and the creation of complex, precise designs (Fig. 5.7) that would be difficult or even impossible using traditional manufacturing methods. The use of

FIGURE 5.7 3D printing of designs with many details. *(Photo taken during 3D Printing Days in Kielce September 24, 2020).*

AM not only enables the delivery of personalized and unique products to customers, but also reduces supply chain costs, and allows products to be delivered in small quantities in a short period of time.

In culture and art, thanks to 3D scanners and 3D printers, it is possible to preserve endangered, destroyed, or lost cultural artifacts and create physical replicas of them [52]. This is used in museology, archaeology, or palaeontology where 3D models of artifacts and monuments are created which can, for example, have educational applications and be made available to visitors without fear of destroying the valuable artifact. Another idea of using 3D printing is the creation of personalized gadgets in a museum shop.

In industrial design, new everyday products under development (Fig. 5.8) are 3D printed at the prototype, mock-up, or final design stage [53]. Furthermore, consumer goods tailored to individual consumer needs are an important application area for 3D printing.

In the fashion industry, prototypes can be created as well as personalized clothing, smart and functional textiles, and artistic designs can be produced. Using 3D printing technology, garments can be designed and produced using a mesh system, combining individual printed components, as well as printing ornaments for traditional textiles [54–56]. AM is also used to produce shoes for athletes or custom-made footwear [57]. Moreover, not only clothes and shoes, but also jewelery and various fashion accessories can be manufactured using AM technology [14,58].

In fashion and textile printing, six technologies have great application potential, namely: SLS, FDM, DIW, SLA, BJT, and PolyJet. The materials used are usually polymers and polymer composites, and among them mainly PA, PLA, TPU, and various inks (colloidal gels, viscous organic fugitive inks, hydrogel inks, and concentrated polyelectrolyte complexes) [28,54–56,58,59].

Jewelery can be manufactured by direct and indirect AM methods. Almost all AM technologies can be used, with particular relevance being: Selective Laser Melting (SLM) and Electron Beam Melting (EBM) for direct manufacturing of jewelery from metal powder and SLA, DLP, FDM, SLS, PolyJet, and BJT for indirect manufacturing. The indirect method can produce either master patterns used for investment casting or direct manufacturing of molds and cores for casting. Unlike textiles, the range of materials used in AM manufacturing is large and besides polymers, metals (stainless steel, gold, silver, bronze, brass, titanium, etc.) as well as wax are the main applications [58,60,61].

5.2.9 AM *processes in marketing, entertainment, and hobbies*

The use of 3D printing in marketing activities is not only its application in printing promotional and advertising materials (Fig. 5.9) or personalized products, but also the usage of 3D scanning and 3D printing in advertising campaigns implemented by well-known brands (e.g., Nokia, Volkswagen, Coca-Cola, Porsche, Honda) [62,63]. Moreover, large-format 3D printing is increasingly used for visual communication to create, e.g., trade fair displays,

FIGURE 5.8 Large-format 3D printing of a vase. *(Photo taken during 3D Printing Days in Kielce September 24, 2020).*

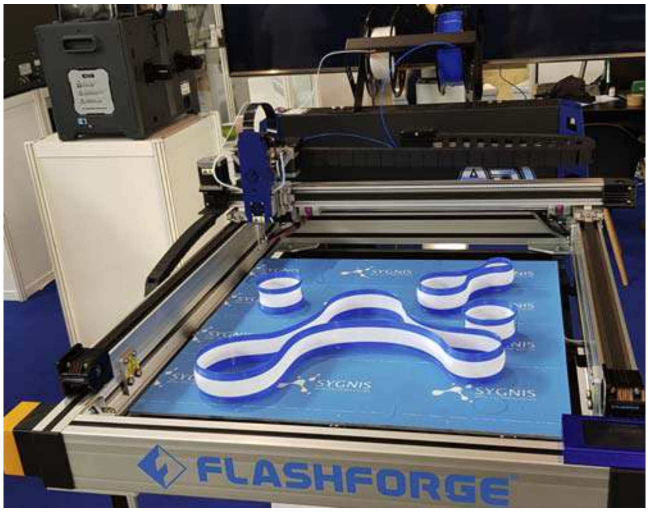

FIGURE 5.9 3D printing of neon letters used in signs and advertising logos. *(Photo taken during 3D Printing Days in Kielce September 24, 2020).*

trade marketing creative elements, props, displays, or signage in 3D. FDM, SLS, SLA, PolyJet, and various polymers as materials are mainly used in marketing activities.

The popularization of AM technology and the availability of affordable 3D printers have led to widespread use of these technologies in design for the entertainment industry (e.g., props, equipment, items for theater, television, film, museums, shop windows) (Fig. 5.10) and hobbyist printing at home by individual users. Self-made 3D prints are shaping new trends and influencing existing understandings of popular culture, as they bypass traditional mass production. Moreover, making and consuming objects on demand is greatly facilitated and enabled by online 3D printing file sharing platforms [64,65].

FIGURE 5.10 3D printed violin. *(Photo taken during 3D Printing Days in Kielce September 24, 2020).*

5.3 Main AM technologies and their applications

According to the data presented in Chapter 3, currently the most important AM technologies using polymers are FDM/FFF, SLA, and SLS, while DLP and MJT technologies are predicted to have the highest growth in market share in the coming years. Due to their significant use in the market, these five technologies will be discussed in the context of their use in different areas and by different industries.

FDM/FFF technologies are mainly used for prototyping, but they are also widely used in R&D departments, in architectural and design offices, and in medicine and industry. Moreover, due to the low cost of a 3D printer and its simple construction, it is the main technology of choice for hobbyists who print their own models or finished designs at home. The use of FDM/FFF technology is actually not limited by the type of industry, but only by the availability of materials and the possibility of their use with a given 3D printer.

SLA technology is used for rapid prototyping and creation of single demonstration models and small-scale production of models with complex geometry. It is used in medicine, design, and industrial design, and due to its high accuracy it is also used to create molds for vacuum casting and in industry, such as aerospace, automotive, jewelery, and dental applications.

DLP technology is used in both prototyping and model making. It is used in industries where high precision and quality are required. DLP is most commonly used in the medical, jewelery, and electronics industries, but it also works well in the creation of injection molds.

SLS technology is used primarily in the production of individual and low-volume parts. Its application is related to the required and achievable high strength of the printed parts, while at the same time high precision of the manufactured parts. SLS is widely used in the automotive and aerospace industries, heavy industry, as well as in robotics and all R&D departments, where the quality of the print matters and the prototype is not just a visualization.

MJP technology is mainly used for prototyping and model testing/proving design concepts. It makes it possible to create parts in a simple way, at high resolution and in a short time. MJP is particularly applicable in dentistry, but is also used in medicine and design work.

5.4 Conclusions

The 3D printing market is rapidly developing and changing. The range of applications and opportunities for the use of AM processes will continue to change with the increasing capabilities of constantly developing and newly emerging technologies. Also, the development of new materials will have a significant impact on future directions of AM technology application. Current professional applications of AM include prototyping to accelerate new product development and low-volume and one-off production of parts. With this, the use of AM for the production of parts or goods is expected to increase further over the coming years. Furthermore, the plethora of materials, technologies, and equipment available on the market means that companies are increasingly shifting from investing in their own equipment to using online manufacturing platforms.

Today, the use of AM technology is very versatile and continues to grow rapidly. This applies to industries such as automotive, aerospace, medical, food, textile, consumer goods, etc. It is changing the product supply chain and developing new products. This trend is expected to continue in the next few years.

Currently, the use of AM technology seems to be particularly relevant in the biomedical field, where unique patient-specific products are often required. This area of application has been developing rapidly in the last few years and will undoubtedly be further developed. Another direction of development for AM applications is and will be the production of individualized functional products, the use of smart materials, and 4D printing.

References

[1] S. Wickramasinghe, T. Do, P. Tran, FDM-based 3D printing of polymer and associated composite: a review on mechanical properties, defects and treatments, Polymers 12 (2020) 1529, https://doi.org/10.3390/polym12071529.

[2] L. Columbus, The State of 3D Printing, 2019. https://www.forbes.com/sites/louiscolumbus/2019/05/27/the-state-of-3d-printing-2019/?sh=3e02166b46c2 (Accessed 27 May 2019).

[3] HUBS, 3D Printing Trends 2020. Industry Highlights and Market Trends, 2020, https://downloads.hubs.com/3D_printing_trends_report_2020.pdf (Accessed 27 May 2021).

[4] J. Dulchinos, 3D Printing Trends: Six Major Developments, 2021, https://www.jabil.com/blog/3d-printing-trends-show-positive-outlook.html (Accessed 27 June 2021).

[5] Sculpteo, Sculpteo Publishes State of 3D Printing 2020 Survey: 3D Printing for Production Increases − 3D Printing Industry, 2020, https://3dprintingindustry.com/news/sculpteo-publishes-state-of-3d-printing-2020-survey-3d-printing-for-production-increases-172216/#:~:text=The%20State%20of%203D%20Printing%3A%20Key%20findings%20Key,a%2050%20percent%20increase%20in%20investments%20this%20year. (Accessed 27 June 2021).

[6] J. van Rensburg (Ed.), Wohlers Report 2021. 3D Printing and Additive Manufacturing State of the Industry, Wohlers Associates, Inc., 2021.

[7] Wohlers Report 2017, Additive Manufacturing and 3D Printing State of the Industry. Annual Worldwide Progress Report, Wohlers Associates, Inc., 2017.

[8] I. Jasiuk, D.W. Abueidda, C. Kozuch, S. Pang, F.Y. Su, J. Mckittrick, An overview on additive manufacturing of polymers, J. Occup. Med. 70 (3) (2018) 275−283.

[9] T.D. Ngo, A. Kashani, G. Imbalzano, K.T.Q. Nguyen, D. Hui, Additive manufacturing (3D printing): a review of materials, methods, applications and challenges, Compos. B Eng. 143 (2018) 172−196, https://doi.org/10.1016/j.compositesb.2018.02.012.

[10] Aerospace and Defense Manufacturing Trends, A Survey of Aerospace and Defense OEMs, Jabil, 2019.

[11] C.W.J. Lim, K.Q. Le, Q. Lu, C.H. Wong, An overview of 3-D printing in the manufacturing, aerospace, and automotive industries, IEEE Potentials 35 (4) (2016) 18−22.

[12] M. Kalender, S.E. Kılıç, S. Ersoy, Y. Bozkurt, S. Salman, Additive manufacturing and 3D printer technology in Aerospace industry, in: 9th International Conference on Recent Advances in Space Technologies (RAST), 2019, https://doi.org/10.1109/RAST.2019.8767881.

[13] S.C. Joshi, A.A. Sheikh, 3D printing in aerospace and its long-term sustainability, Virtual Phys. Prototyp. 10 (4) (2015) 175−185, https://doi.org/10.1080/17452759.2015.1111519.

[14] N. Shahrubudin, T.C. Lee, R. Ramlan, An overview on 3D printing technology: technological, materials, and applications, Procedia Manuf. 35 (2019) 1286−1296.

[15] L.J. Kumar, C.G. Krishnadas Nair, Current trends of additive manufacturing in the aerospace industry, in: D. Wimpenny, P. Pandey, L. Kumar (Eds.), Advances in 3D Printing & Additive Manufacturing Technologies, Springer, Singapore, 2017, https://doi.org/10.1007/978-981-10-0812-2_4.

[16] A.D. Valino, J.R.C. Dizon, A.H. Espera, Q. Chen, J. Messman, R.C. Advincula, Advances in 3D printing of thermoplastic polymer composites and nanocomposites, Prog. Polym. Sci. 98 (2019) 101162, https://doi.org/10.1016/j.progpolymsci.2019.101162.

[17] S. Yuan, F. Shen, C.K. Chua, K. Zhou, Polymeric composites for powder-based additive manufacturing: materials and applications, Prog. Polym. Sci. 91 (2019) 141−168, https://doi.org/10.1016/j.progpolymsci.2018.11.001.

[18] A. Lele, Chapter 5. Additive manufacturing (AM), in: Disruptive Technologies for the Militaries and Security, Smart Innovation, Systems and Technologies, vol. 132, Springer, Singapore, 2019, pp. 101−109, https://doi.org/10.1007/978-981-13-3384-2_5.

[19] I. Bahnini, M. Rivette, A. Rechia, A. Siadat, A. Elmesbahi, Additive manufacturing technology: the status, applications, and prospects, Int. J. Adv. Manuf. Technol. 97 (2018) 147−161, https://doi.org/10.1007/s00170-018-1932-y.

[20] M. Chinthavali, 3D printing technology for automotive applications, in: International Symposium on 3D Power Electronics Integration and Manufacturing (3D-PEIM), Conference Paper, IEEE, 2016.

[21] M.R. Nichols, How does the automotive industry benefit from 3D metal printing? Met. Powder Rep. 74 (5) (2019) 257−258, https://doi.org/10.1016/j.mprp.2019.07.002.

[22] M. Savastano, C. Amendola, F. D′Ascenzo, E. Massaroni, 3-D printing in the spare parts supply chain: an explorative study in the automotive industry, in: L. Caporarello, F. Cesaroni, R. Giesecke, M. Missikoff (Eds.), Digitally Supported Innovation, Lecture Notes in Information Systems and Organisation, vol. 18, Springer, Cham, 2016, https://doi.org/10.1007/978-3-319-40265-9_11.

[23] O.F. Beyca, G. Hancerliogullari, I. Yazici, Chapter 13. Additive manufacturing technologies and applications, in: A. Ustundag, E. Cevikcan (Eds.), Industry 4.0: Managing the Digital Transformation, Springer Series in Advanced Manufacturing, Springer International Publishing, Cham, 2018, https://doi.org/10.1007/978-3-319-57870-5_13.

[24] J.-Y. Lee, J. An, C.K. Chua, Fundamentals and applications of 3D printing for novel materials, Appl. Mater. Today 7 (2017) 120−133, https://doi.org/10.1016/j.apmt.2017.02.004.

[25] G.L. Goh, S. Agarwala, W.Y. Yeong, Directed and on-demand alignment of carbon nanotube: a review toward 3D printing of electronics, Adv. Mater. Interfac. 6 (4) (2019) 1801318, https://doi.org/10.1002/admi.201801318.

[26] H.W. Tan, J. An, C.K. Chua, T. Tran, Metallic nanoparticle inks for 3D printing of electronics, Adv. Elect. Mater. 5 (5) (2019) 1800831, https://doi.org/10.1002/aelm.201800831.

[27] M. Abshirini, M. Charara, P. Marashizadeh, M.C. Saha, M.C. Altan, Y. Liu, Functional nanocomposites for 3D printing of stretchable and wearable sensors, Appl. Nanosci. 9 (2019) 2071−2083, https://doi.org/10.1007/s13204-019-01032-2.

[28] Q. Wang, J. Sun, Q. Yao, C. Ji, J. Liu, Q. Zhu, 3D printing with cellulose materials, Cellulose 25 (2018) 4275–4301, https://doi.org/10.1007/s10570-018-1888-y.

[29] A. Ambrosi, M. Pumera, 3D-printing technologies for electrochemical applications, Chem. Soc. Rev. 45 (2016) 2740–2755.

[30] M. Ziaee, N.B. Crane, Binder jetting: a review of process, materials, and methods, Addit. Manuf. 28 (2019) 781–801, https://doi.org/10.1016/j.addma.2019.05.031.

[31] R.S. Jordan, Y. Wang, 3D printing of conjugated polymers, J. Polym. Sci. B Polym. Phys. 57 (2019) 1592–1605, https://doi.org/10.1002/polb.24893.

[32] O. Chandran, S. Lani, D. Briand, B. Dunan, G. Voirin, Additive manufacturing on 3D surfaces, in: M. Meboldt, C. Klahn (Eds.), Industrializing Additive Manufacturing – Proceedings of Additive Manufacturing in Products and Applications – AMPA2017, Springer International Publishing AG, 2018, https://doi.org/10.1007/978-3-319-66866-6_13.

[33] Y.Y.C. Choong, H.W. Tan, D.C. Patel, W.T.N. Choong, C.-H. Chen, H.Y. Low, M.J. Tan, C.D. Patel, C.K. Chua, The global rise of 3D printing during the COVID-19 pandemic, Nat. Rev. Mater. 5 (2020) 637–639.

[34] G.R.J. Swennen, L. Pottel, P.E. Haers, Custom-made 3D-printed face masks in case of pandemic crisis situations with a lack of commercially available FFP2/3 masks, Int. J. Oral Maxillofac. Surg. 49 (5) (2020) 673–677, https://doi.org/10.1016/j.ijom.2020.03.015.

[35] A. Aimar, A. Palermo, B. Innocenti, The role of 3D printing in medical applications: a state of the art, J. Healthc. Eng. 2019 (2019) 5340616, https://doi.org/10.1155/2019/5340616.

[36] S. Beg, W.H. Almalki, A. Malik, M. Farhan, M. Aatif, Z. Rahman, N.K. Alruwaili, M. Alrobaian, M. Tarique, M. Rahman, 3D printing for drug delivery and biomedical applications, Drug Discov. Today 25 (9) (2020) 1668–1681, https://doi.org/10.1016/j.drudis.2020.07.007.

[37] H.N. Chia, B.M. Wu, Recent advances in 3D printing of biomaterials, J. Biol. Eng. 9 (4) (2015) 25866560, https://doi.org/10.1186/s13036-015-0001-4.

[38] G.-H. Wu, S-h. Hsu, Review: polymeric-based 3D printing for tissue engineering, J. Med. Biol. Eng. 35 (2015) 285–292, https://doi.org/10.1007/s40846-015-0038-3.

[39] R. Di Gesù, A.P. Acharya, I. Jacobs, R. Gottardi, 3D printing for tissue engineering in otolaryngology, Connect. Tissue Res. 61 (2) (2020) 117–136, https://doi.org/10.1080/03008207.2019.1663837.

[40] O. Diegel, A. Nordin, D. Motte, Chapter 13. The future of additive manufacturing, in: A Practical Guide to Design for Additive Manufacturing, Springer Series in Advanced Manufacturing, Springer, Singapore, 2020, pp. 209–216, https://doi.org/10.1007/978-981-13-8281-9_13.

[41] P. Robles Martinez, Pharmaceutical Applications of Stereolithography (SLA) 3D Printing, Doctoral thesis (Ph.D), UCL (University College London), 2019.

[42] A. Awad, F. Fina, A. Goyanes, S. Gaisford, A.W. Basit, 3D printing: principles and pharmaceutical applications of selective laser sintering, Int. J. Pharm. 586 (2020) 119594, https://doi.org/10.1016/j.ijpharm.2020.119594.

[43] P. Vasamsetty, T. Pss, D. Kukkala, M. Singamshetty, S. Gajula, 3D printing in dentistry – exploring the new horizons, Mater. Today Proc. 26 (2) (2020) 838–841, https://doi.org/10.1016/j.matpr.2020.01.049.

[44] D. Khorsandi, A. Fahimipour, P. Abasian, S.S. Saber, M. Seyedi, S. Ghanavati, A. Ahmad, A.A. De Stephanis, F. Taghavinezhaddilami, A. Leonova, R. Mohammadinejad, M. Shabani, B. Mazzolai, V. Mattoli, F.R. Tay, P. Makvandi, 3D and 4D printing in dentistry and maxillofacial surgery: printing techniques, materials, and applications, Acta Biomater. 122 (2021) 26–49, https://doi.org/10.1016/j.actbio.2020.12.044.

[45] M. Walker, S. Humphries, 3D printing: applications in evolution and ecology, Ecol. Evol. 9 (2019) 4289–4301, https://doi.org/10.1002/ece3.5050.

[46] K. Govil, V. Kumar, D.P. Pandey, R. Praneeth, A. Sharma, Additive manufacturing and 3D printing: a perspective, in: A. Prasad, et al. (Eds.), Advances in Engineering Design, Lecture Notes in Mechanical Engineering, Springer, Singapore, 2019, pp. 321–334, https://doi.org/10.1007/978-981-13-6469-3_29.

[47] T. Leinonen, M. Virnes, I. Hietala, J. Brinck, 3D printing in the wild: adopting digital fabrication in elementary school education, Int. J. Art Des. Educ. 39 (3) (2020) 600–615, https://doi.org/10.1111/jade.12310.

[48] R. Mathur, 3D printing in architecture, Int. J. Innovat. Sci. Eng. Technol. 3 (7) (2016) 583–591.

[49] M.P.A.M. Marijnissen, A. van der Zee, 3D concrete printing in architecture. A research on the potential benefits of 3D concrete printing in architecture, in: Proceedings of the 35th International Conference on Education and Research in Computer Aided Architectural Design in Europe, Rome, Italy, 20th–22nd September 2017, Material Studies – Methodologies, Vol. 2, eCAADe, 2017, pp. 299–308.

[50] C.-H. Ko, Constraints and limitations of concrete 3D printing in architecture, J. Eng. Des. Technol. (2021), https://doi.org/10.1108/JEDT-11-2020-0456.

[51] L. Chen, Y. He, Y. Yang, S. Niu, H. Ren, The research status and development trend of additive manufacturing technology, Int. J. Adv. Manuf. Technol. 89 (2017) 3651–3660, https://doi.org/10.1007/s00170-016-9335-4.

[52] C. Elias, Whose digital heritage? Third Text 33 (6) (2019) 687–707, https://doi.org/10.1080/09528822.2019.1667629.

[53] S. Adamczak, M. Graba, The 3D printing in industrial design, Mechanik 1 (2020) 21–26, https://doi.org/10.17814/mechanik.2020.1.1.

[54] R. Melnikova, A. Ehrmann, K. Finsterbusch, 3D printing of textile-based structures by fused deposition modelling (FDM) with different polymer materials, IOP Conf. Ser. Mater. Sci. Eng. 62 (2014) 012018, https://doi.org/10.1088/1757-899X/62/1/012018.

[55] T. Spahiu, N. Grimmelsmann, A. Ehrmann, E. Piperi, E. Shehi. Effect of 3D printing on textile fabric, Proceedings of 1st International Conference "Engineering and Entrepreneurship", Tirana, Albania, November 2017, ICEE, 2017, pp. 1–7.

[56] A. Vanderploeg, S.-E. Lee, M. Mamp, The application of 3D printing technology in the fashion industry, Int. J. Fash. Des. Technol. Educ. 10 (2) (2017) 170–179, https://doi.org/10.1080/17543266.2016.1223355.

[57] T. Spahiu, E. Piperi, A. Ehrmann, H.A. Almeida, R.M.T. Ascenso, L.C. Vitorino, 3D printing: an innovative technology for customised shoe manufacturing, in: H. Almeida, J. Vasco (Eds.), Progress in Digital and Physical Manufacturing. ProDPM 2019. Lecture Notes in Mechanical Engineering, Springer, Cham, 2020, pp. 171–180, https://doi.org/10.1007/978-3-030-29041-2_22.

[58] Y.L. Yap, W.Y. Yeong, Additive manufacture of fashion and jewellery products: a mini review, Virtual Phys. Prototyp. 9 (3) (2014) 195–201, https://doi.org/10.1080/17452759.2014.938993.

[59] K. Chatterjee, T.K. Ghosh, 3D printing of textiles: potential roadmap to printing with fibers, Adv. Mater. 32 (4) (2020) 1902086, https://doi.org/10.1002/adma.201902086.

[60] Y. Zhai, D.A. Lados, J.L. Lagoy, Additive manufacturing: making imagination the major limitation, J. Occup. Med. 66 (5) (2014) 808−816, https://doi.org/10.1007/s11837-014-0886-2.

[61] B. Duan, Analysis on the value of 3D printing in jewelry design based on artificial intelligence, J. Phys. Conf. Ser. 1744 (2021) 042132.

[62] D. Chaney, J. Gardan, J. De Freyman, A framework for the relationship implications of additive manufacturing (3D printing) for industrial marketing: servitization, sustainability and customer empowerment, J. Bus. Ind. Market. 37 (2021), https://doi.org/10.1108/JBIM-04-2020-0207.

[63] W. Wu, S.B. Tor, 3D printing for marketing and advertisement industry, in: Proceedings of the 1st International Conference on Progress in Additive Manufacturing (Pro-AM 2014), 2014, pp. 303−308.

[64] A.E. McMills, 3D Printing Basics for Entertainment Design, first ed., Routledge, New York, NY, 2017 https://doi.org/10.4324/9781315108698.

[65] J.I. Novak, P. Bardini, Chapter 12. The popular culture of 3D printing: when the digital gets physical, in: Handbook of Research on Consumption, Media, and Popular Culture in the Global Age, IGI Global Publishing House, 2019, pp. 188−211, https://doi.org/10.4018/978-1-5225-8491-9.ch012.

PART II

3D printing methods

C H A P T E R

6

Vat photopolymerization

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6.1 Introduction

Vat photopolymerization is a collective name for the additive manufacturing processes in which liquid photopolymer in a vat (large tank or tub used to hold liquid) is selectively cured by selectively activated polymerization [1]. This group of additive manufacturing processes (AM) is also known as photolithographic 3D printing or resin 3D printing.

Vat photopolymerization processes could be classified into the four most used groups:

1. Stereolithography apparatus (SLA),
2. Digital light processing (DLP),
3. Digital light synthesis (DLS) also known as continuous liquid interface production (CLIP),
4. Liquid crystal display (LCD 3D printing) also known as daylight polymer printing (DPP).

All the processes rely on the same basic strategy: a liquid photopolymer contained in a vat is selectively cured layer by layer or point by point using a directed radiation source. Vat photopolymerization processes offer great variety of choice regarding the apparatus construction, material characteristics, and polymerization process parameters, so all of the parameters must be carefully examined in order to get satisfying results of the 3D printing process. Different chemical composition of the photopolymer resins can affect appearance, tensile and flexural strength, elongation at break, Shore D hardness, water absorption, adhesion, and other properties of the produced object. Resins used in stereolithography are commonly composed of acrylate, epoxide, or vinyl ether monomers/oligomers [2] which are core of the resin that will make up the solid parts, photoinitiator that reacts to UV light initiating the reaction, and additives which are visual and functional supplements, such as pigments or dyes. Depending on the desired characteristics and intended use of the produced object basic resins can be divided into several basic groups:

1. standard resin,
2. clear resin,
3. castable resin,
4. tough or durable resin,
5. high-temperature resin,
6. dental resin,
7. rubber-like resin,
8. custom resins.

Radiation sources differ depending on the technology:

1. laser emission,
2. single light bulb, conventional, or LED,
3. array of LEDs,
4. electromagnetic radiation generators.

Polymers for 3D Printing
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Polymer resins used in 3D printing can be solidified by different radiation:

1. ultraviolet (UV),
2. visible light range of wavelengths,
3. infrared (IR),
4. gamma rays,
5. X-rays,
6. electron beams.

There are also different approaches to directing the light photons to the desired area in a very precise and controlled manner. Processes in the vat photopolymerization group could be classified according to this parameter:

1. vector scan, or pointwise polymerization,
2. mask projection, or layerwise polymerization,
3. two-photon polymerization (TPP), high-resolution point-by-point polymerization.

Construction of the machines should ensure precise control of the moving parts. Solidification of the resin is happening on the interface between the last solidified layer and the surface of the new layer of resin in most of the processes. Some systems use mechanical movement in all three axes (*X*, *Y* and *Z*) to ensure positioning of the radiation beam, while some of them mechanically move on the *Z*-axis while *X*, *Y* coordinates are controlled by directing the radiation. There are two mainstream approaches of object manufacturing top-down also known as free surface method and bottom-up fixed surface method depending on the direction of movement on *Z*-axis [3]. A different approach is taken in TPP processes, as the resin is solidified in the middle of the vat.

6.2 Brief historical overview

A recent development in computer technology gave rise to virtual 3D modeling and precise control of machinery needed for efficient production of 3D printed objects. This fact is crucial for all the AM processes as all of them are based on the same principle where the process begins with a creation of the digital 3D model, which is a representation of the physical object in the virtual 3D world. Dedicated software slices the 3D model into two-dimensional layers with defined thickness. The thickness of the layer depends on the machine capabilities and process parameters, defining the precision of the object and time needed for production. One slice produced in this process is turned into G-code, which is a set of instructions for the machine needed for the production of the layer in the *X*, *Y* plane. After production of one layer, object is usually moved on *Z*-axis leaving the room for the next layer to be produced. Continuous repetition of this process results in creation of 3D object.

Besides the development of computer technology, development of vat photopolymerization processes is closely tied to the development of the photopolymerization process and development of suitable materials and technologies.

Photosensitive materials have been known and used from ancient times. Phenomena of blackening silver salts by light exposure was known in middle ages but it was explained as an effect of the heat produced by the sunlight and not only the light itself. Later understanding of the process by Schultz (1775) and Niepce (1822) propelled the development of numerous processes based on the polymerization process [4]. During 1950 and 1960s significant advancements were made in the chemical composition of the photosensitive polymers, paving the way for diverse usage of this technology.

Battelle Memorial Institute was the first to attempt manufacturing solid objects by intersecting two laser beams of differing wavelength in the middle of a vat of polymer resin, solidifying the material at the point of intersection in the 1960s [5]. Modern photolithographic AM systems started to emerge during the 1970s. The major push in the technology development was done by numerous patents by Wyn Swainson of Formigraphic Engine Co. His patent from 1971 describes the apparatus in which a three-dimensional object is formed in a medium by intersecting two radiation beams in the media. Problems with the absorption of the photons by the media and its polymerization along the beam path were addressed in later patents by Swainson during 1980s, although it was never developed into the commercially available system [6–9]. Hideo Kodama of Nagoya Municipal Industrial Research Institute developed the foundational methodology of using the cross-sectional slices of a model for layered production of 3D objects using single-beam laser technology. This technology can still be found in many modern SLA 3D printers. Kodama explained "If the solidified layer is immersed into the liquid with the top at a depth equal to the thickness of the layer to be solidified, its top surface is covered with unsolidified liquid polymer," which is key principle of the stereolithography process, but it was never realized as a viable product [8]. Alan Herbert of 3M Graphic Technologies Sector Laboratoryp (1982) was able to create small 3D objects of basic shapes by using a mirror system to direct an Argon Ion laser beam onto the surface of photopolymer [9,10].

Charles Hull of 3D Systems is known today as the inventor of stereolithography. Hull's patent (1986) is based on a process of polymerizing a series of individual cross-sections using a computer-controlled beam of light [11,12]. Jean-Claude André of the French National Center for Scientific Research with a group of researchers worked on similar principle [13,14]. While André's patent application was rejected and the project was stopped due to lack of funding, Hull started his own company in 1986, called 3D Systems and released the first commercial product, the SLA-1, in 1988. In the second half of the 1980s, there were few very important patents to improve deposition of the liquid polymer resin. Takashi Morihara of Fujitsu Ltd. introduced the blade for leveling the new layer of resin, which is essential for viscous resins. Second Morihara's solution was the dispersion of the resin from a slot moving above the surface of the printed object and the resin [5]. Larry Hornbeck of Texas Instruments (1986) patented DLP technology which uses digital micromirrors laid out on a semiconductor chip [15]. First AM machine using DLP technology was constructed by Bertschs research team [16]. Takafumi Nakayama of Sanyo Electric developed and patented usage of a flat LCD panel as a discrete mask through which light would pass onto the surface of photopolymer resin [17]. DLS technology owned by Carbon 3D introduced process capable of continuously printing objects due to the clear bottom acting as an oxygen-permeable membrane which inhibits solidification of the resin within a certain zone around the bottom of the vat. This increased printing speeds 25−100 times compared to other layer-by-layer AM processes [18]. Late 1980s and early 1990s were dynamic times where significant steps were made in the commercialization of this technology by big companies such as 3D Systems, Quadrax, Mitsubishi Heavy Industries, DuPont, etc. [5]. These early AM systems were embraced predominantly by the automobile industry. During following years photolithographic processes got respectable competition in other technologies which were in some cases more affordable, offered specific advantages as mechanical strength of the parts or possibility to produce objects using multiple colors. With the expiration of the patents during the second half of 2000s AM machines got fairly assessable; this was not the case for stereolithography as nobody had been able to create affordable SLA system. With the popularization of funding platforms such as Kickstarter, Company B9 Creator (2012) managed to receive funding and produced affordable device, priced under 3000 USD, based on DLP technology. Not much later Company Formlabs managed to produce similarly priced 3D printed utilizing SLA technology. Today's market of 3D printers based on the photolithographic process is extremely diverse offering machines based on SLA, DLP, and LCD technology, varying in build volume, speed, precision, with prices reaching as low as 200 USD.

6.3 Stereolithography apparatus

Stereolithography is not only the oldest among vat photopolymerization processes but it is generally first conceived principle 3D printing soon followed by the other AM techniques. Long time SLA was synonymous with the vat photopolymerization, often today authors use it as the name for the whole class of the AM techniques based on photopolymerization. Despite being the oldest it is arguably still the most precise process for the creation of finely detailed parts. This is achieved by constant improvement of the technology. The objects are created by local polymerization of the initially liquid resin using laser beam emitting the UV light ranging from wavelength from 350 nm up to 460 nm, but most often in the range between 385 and 405 nm. The laser beam is precisely controlled and directed by a computer-guided mirror onto the surface of the photopolymer resin according to the contour of each layer defined in G-code. As polymerization turns the liquid into a solid the object is built one layer at a time.

SLA machine can be divided into three basic parts:

1. power and control unit,
2. imaging unit,
3. build unit.

Power and control unit provides the energy needed for the operation of electronics, laser, and drive mechanisms. Control unit deals with data received from the slicing software on the computer, although today it is customary to include computing unit capable of doing slicing and support generation in the 3D printer itself so it could function as a standalone device.

Imaging unit consists of laser light source providing high power UV light beam, lens system intended for focusing the light beam, and system for laser scanning of the surface in the X, Y axis, thus generating the $X-Y$ contour. As SLA is based on Vector scan or pointwise polymerization, a single point of the resin surface is being exposed to the laser beam at the time. Directing of the laser beam can be achieved by mechanical laser plotters, but today galvo-type scanning is prevalent as it offers faster scanning of the surface. Galvo-type scanning is directing of the laser beam by the motor-driven rotating mirror. Redirection of the laser beam by rotating mirror scanning of the surface can be done in linear fashion producing fine rounded lines around 80 μm in width, and rounded voxels, as shown in Fig. 6.1.

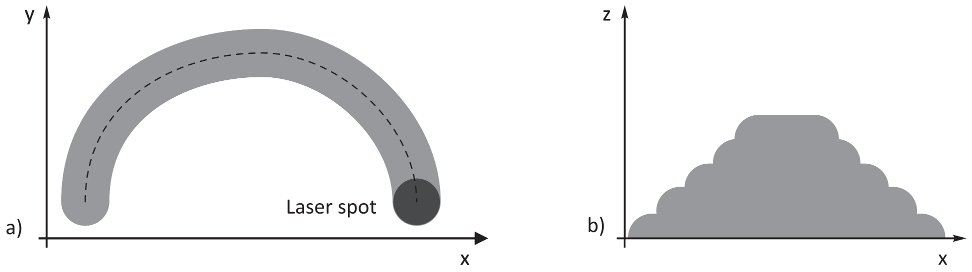

FIGURE 6.1 Shape of the resin solidification by laser in SLA process: (A) view perpendicular to the laser beam and (B) depth cross section of the resin solidification.

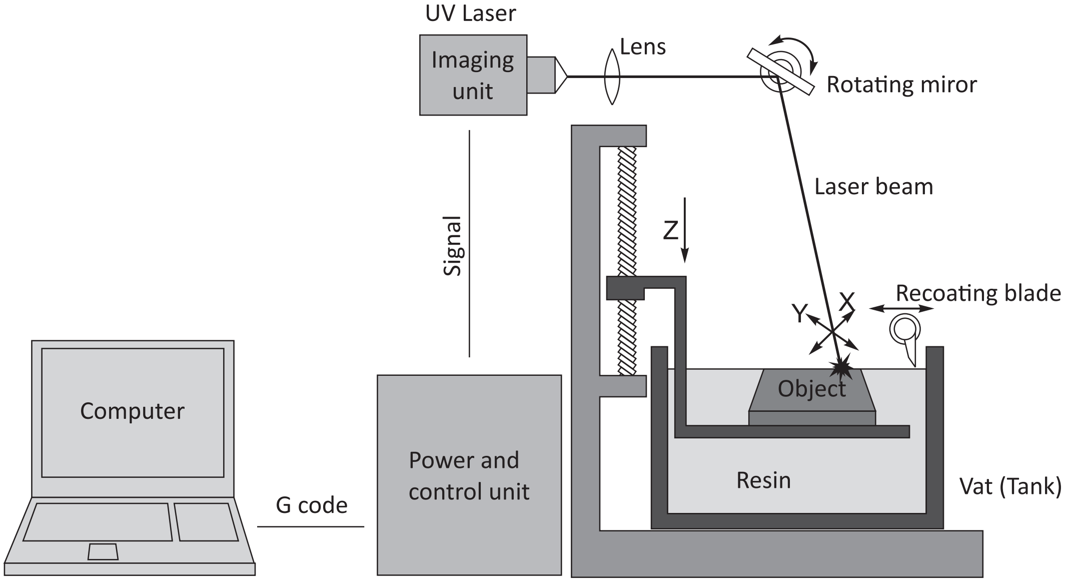

FIGURE 6.2 Schematic view of the SLA machine with top-down approach to construction.

Build unit consists of a resin tank filled with the liquid resin. Inside of the tank the build platform is submerged in the resin. The build platform is connected to the elevator mechanism, usually threaded spindle, which ensures the movement of the platform in the *Z* axis. At the beginning of the printing process platform is submerged in the resin on the depth corresponding to the layer height. As the first layer of the resin is solidified by *X*, *Y* movement of the laser beam elevator system ensures that the object is submerged further in the tank for the height of the next layer. Each interaction of UV light and resin produces solidified volume called a voxel. Height of the layer is defined by the slicer settings and the power of the laser beam. SLA process offers layer height ranging from 25 to 300 μm.

Having in mind viscosity of the resin, it will not evenly cover the surface of the previous layer due to the adsorption. The new layer of resin needs to be applied in the recoating procedure by the recoating blade. This cycle continues until the object is finished. Schematic view of the SLA machine with top-down approach of construction is shown in Fig. 6.2.

After the building process is finished, the residue of the liquid resin needs to be removed from the object, usually by a mixture of isopropyl alcohol and water. Post-curing process using a UV chamber or exposure to sunlight is necessary in order for the polymerization process of the whole structure to be finished. SLA process requires support structure, thus their removal is the part of postprocessing. Depending on the material and desired result, further mechanical or chemical treatment might be needed.

SLA machines that use fixed position rotating mirror suffer from uneven curing across the surface of the resin layer. Formlab introduced Low Force Stereolithography (LFS) 3D printing that delivers a laser beam that is always perpendicular to the build plane, so it is always moving in a straight line to provide even greater precision and accuracy.

6.4 Digital light processing

DLP is mask projection or layerwise polymerization based process. It uses a light source in the UV wavelength range, but in contrast to SLA process which uses a laser, DLP is using UV bulb lamp where the light is not concentrated in the light beam but rather projected on to the digital micromirrors device laid out on a semiconductor chip (DMD chip). Several hundred thousand of 8 μm by 8 μm mirrors are arranged in a rectangular array; this forms the pixels matrix of the projected image. By rotating individual mirrors ±10−12° the light from the UV bulb can be reflected into the lens making the pixel appear bright on the screen or it can be directed elsewhere making the pixel appear dark. To produce light of different intensity the mirrors are toggled on and off very quickly, thus reflecting less light and producing up to 1024 shades. This technology is also used in DLP video projectors for the projection of RGB images [19]. Because of the small scale, mirrors are capable of doing 1 trillion cycles without damage and are very resilient to shock and vibration [20]. By using reflection of the UV light on the microlevel projected image presents the whole cross-section of the object; thus the surface of the layer is cured at once without scanning. After the layer is cured Build platform is moved on *Z*-axis, making space for the liquid resin to fill the gap between the previous layer and transparent screen. In the case of DLP machines layer height is ranging from 35 to 300 μm. Schematic of the DLP machine with a bottom-up approach to construction is shown in Fig. 6.3.

Construction of the DLP machines is similar to the SLA machines, the main difference being the imaging unit. With the implementation of the micromirrors and pixelation of the projected image fine rounded lines seen in case of SLA technology cannot be reproduced. The projected image is pixelated causing some problems in the reproduction of rounded surfaces, especially in the vertical direction (Fig. 6.4). DLP process offers higher speed when printing big objects with some concessions concerning quality, compared to SLA resolution is lower as lines have jagged edges minimal width 100 μm, and rectangular voxels. Accuracy of DLP printers in *X*, *Y* plane is highly dependable on the resolution of the DMD chip.

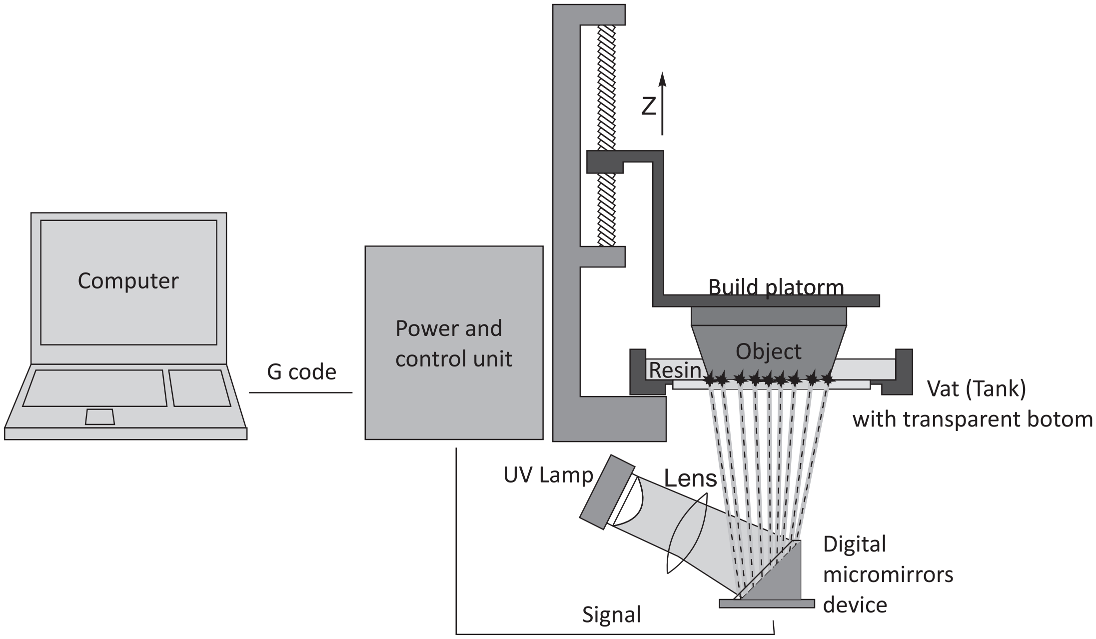

FIGURE 6.3 Schematic view of the DLP machine with bottom-up approach of construction.

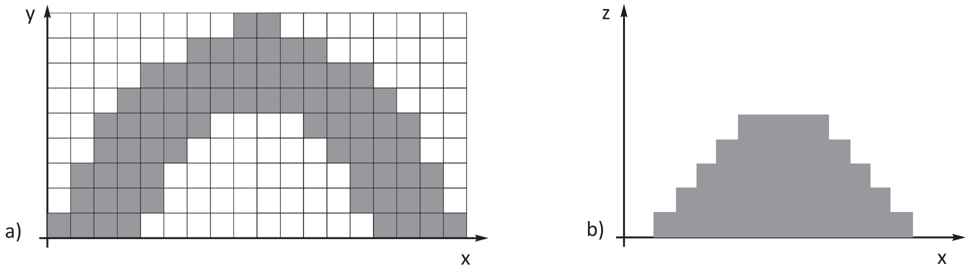

FIGURE 6.4 Shape of the resin solidification by DMD pixel matrix in DLP process: (A) view perpendicular to the radiation source, and (B) depth cross section of the resin solidification.

6.5 Digital light synthesis

DLS also called CLIP is mask projection, or layerwise polymerization based process, and it uses DLP projection principle for light direction. In contrast to conventional DLP process, the UV images are projected in a continuous sequence through an oxygen-permeable, UV-transparent screen (Teflon AF 2400) beneath a liquid resin tank. The oxygen-inhibited dead zone created above the oxygen-permeable window maintains a thin liquid layer below the printed object. Above the dead zone, the object is continuously drawn upward out of the resin, thus creating suction forces that constantly renew liquid resin between the object and the screen. Schematic of the DLS machine with a bottom-up approach to construction is shown in Fig. 6.5.

In contrast to traditional stereolithography bottom-up and top-down approaches where the object is moved in *Z*-axis in discrete steps after the curing process of the layer is finished, DLS enables the continuous building of the object without stopping. The number of slices which significantly increase printing time in other AM processes does not affect print time in this process as it is continuous and the number of projected images can be increased without influence on print speeds. This results in smooth transitions between layers without step effect [18].

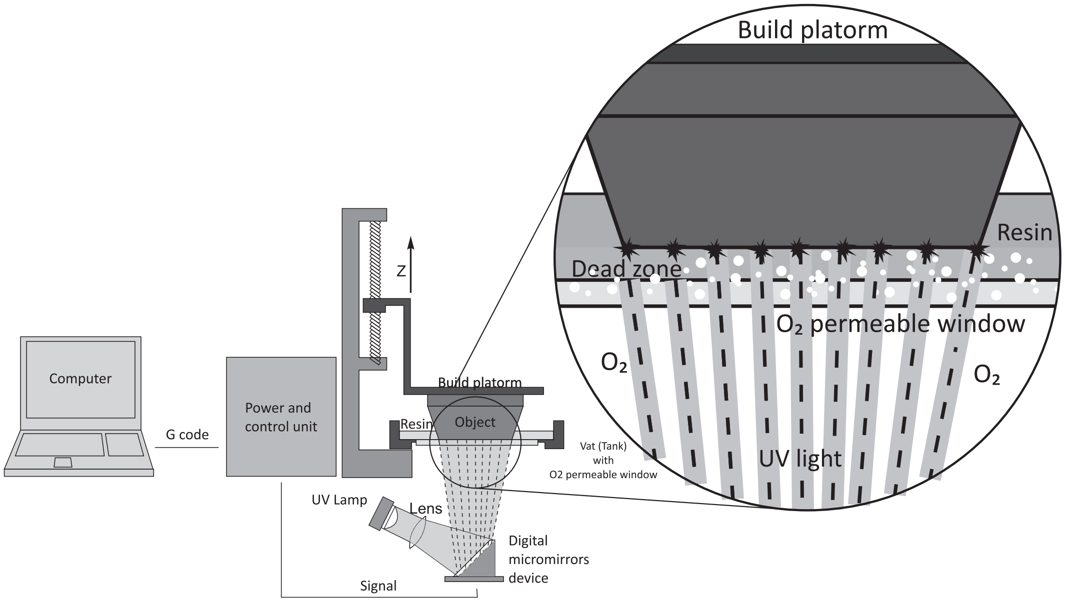

FIGURE 6.5 Schematic view of the DLS machine with bottom-up approach of construction.

6.6 Liquid crystal display (3D printing)

LCD 3D printing also known as DPP is mask projection or layerwise polymerization based process. The LCD screen is a matrix made out of pixels. The number of pixels in one matrix can reach millions, depending on the size of the screen and individual pixel. LCD technology basically controls the passage of the light through the individual pixel by combining liquid crystals, polarized glass, electrical circuitry, and source of the light. Liquid crystals can twist and untwist depending on whether they are electrically charged or not; this changes the frequency of the light passing through them. In combination with polarized glass in front and behind liquid crystal layer flow of light through the assembly can be controlled by sending electrical current. LCD 3D printers use this mechanism to control curing of the resin. Construction of the machine is similar to the DLP machines with the regard that LCD machines use only a bottom-up approach. Schematic of the LCD machine with a bottom-up approach to construction is shown in Fig. 6.6.

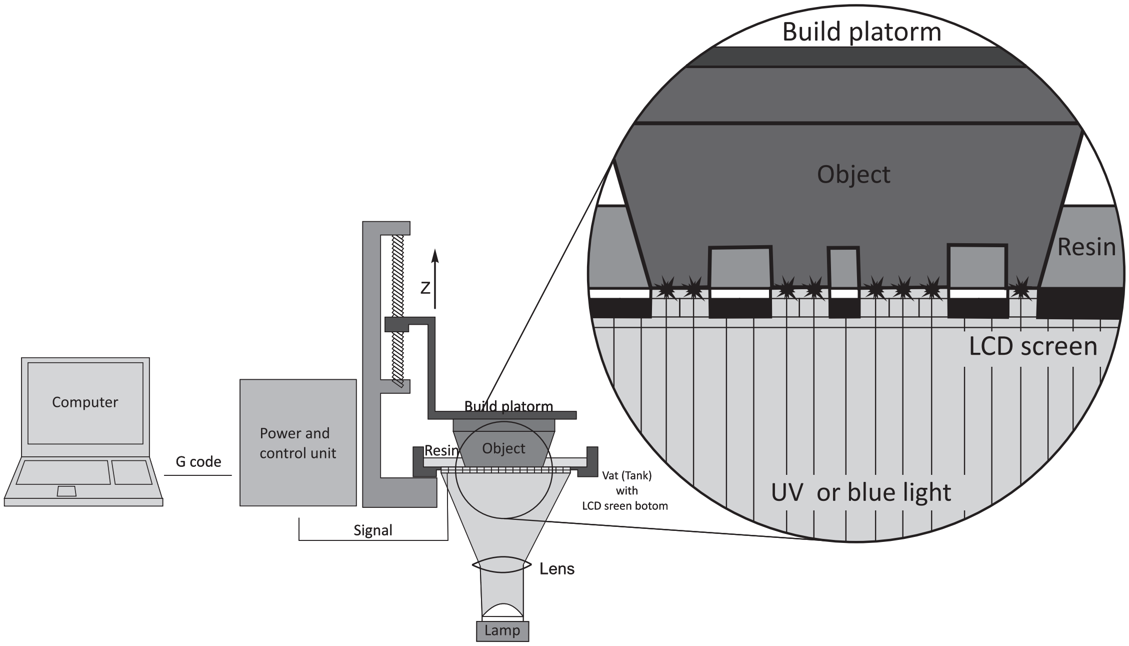

FIGURE 6.6 Schematic view of the LCD machine with bottom-up approach of construction.

6.7 Two-photon photopolymerization

TPP is high-resolution point-by-point polymerization that enables fabrication of 3D objects on micrometer level. Two-photon absorption occurs when the combined energy of two photons matches the transition energy between the ground state and an excited state, which triggers polymerization. This ensures that polymerization is restricted to the area at the focal point. Microstereolithography (MSLA) is the process based on the TPP where the block of the photosensitive gel is used to enable polymerization of the layers composing the object directly inside medium and not on the top or bottom surface. This also eliminates the need for the support structure. Focused femtosecond laser induces a highly localized chemical reaction leading to polymerization of the photosensitive gel only at the focal spot of the laser, where the intensity of the light is highest, producing high precision solidification. Laser scans structure of the object layer by layer, afterward excess gel can be washed away leaving only solidified object. In order to achieve high precision block of the photosensitive gel is moved in all three axes (*X*, *Y*, and *Z*) while laser stays stationary. Very small objects have been built with this process with a submicron resolution, like a microtube having an outside diameter of less than 3 μm and an inside diameter of 1.8 μm [21,22]. Schematic of the TPP process is shown in Fig. 6.7.

6.8 Top-down and bottom-up approaches to 3D printer construction

Machines based on the SLA and DLP principle can be built implementing both top-down and bottom-up approaches, while DLS and DPP machines can implement only as a bottom-up approach due to the process specifics. Schematics of top-down and bottom-up approaches are shown in Fig. 6.8A and B. All aspects of the bottom-up approach are the same as previously explained with the difference of *Z*-axis movement. As the platform is moving up the object is being pulled out of resin rather than being submerged. Scanning is done from beneath through transparent screen. Bottom-up approach (Fig. 6.8B) is gaining popularity as it requires far less resin in the tank. Also, there are no limitations of the build volume caused by the depth of the tank as in the case of the top-down approach. On the other hand, having in mind that during the 3D printing process some solidified resin particles can accrue and foreign free-flowing particles, as well as pigments, can sink to the bottom of the resin tank covering the transparent screen and obstructing the light in the bottom-up approaches, a top-down approach can offer some advantage. A possible problem with bottom-up approach is "vat sticking issue" caused by vacuum force when the platform is moved upward, thus demanding thicker support structure [3]. LFS by Formlabs introduces novelty flexible resin tank which reduces the forces exerted on parts during the print process.

An alternative to these two approaches is solidification in the volume of polymer gel, used in TPP process where the laser is fixed and the half solid photosensitive gel block is moved in all three axes. Polymerization is done inside the volume of the gel block as shown in Fig. 6.8C.

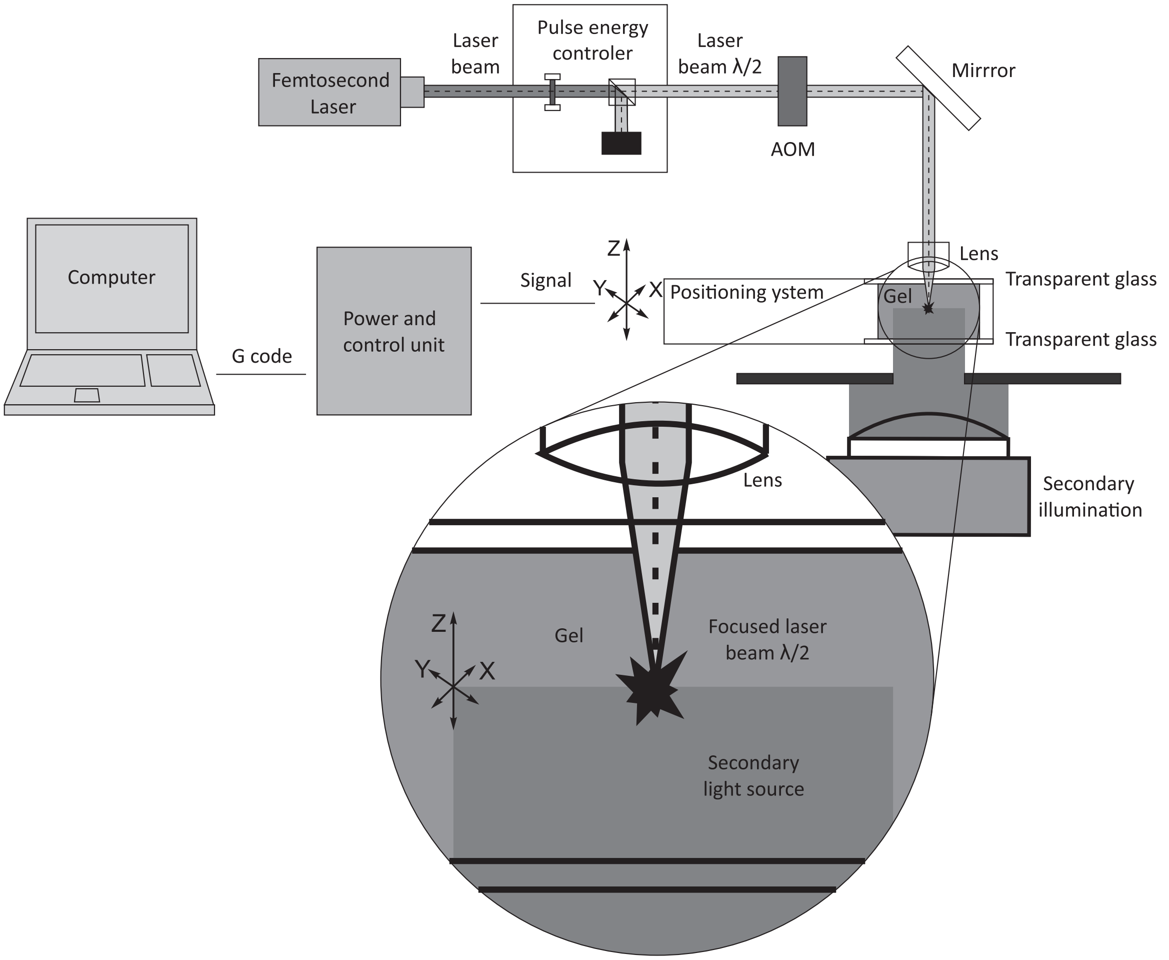

FIGURE 6.7 Schematic view of the TPP process.

6.9 Support structure

As each new layer of the object must be supported by the previous layer and resin used in this processes is liquid and it does not offer support for the overhang or bridged parts of the object which are not supported by the previous layer, it is needed print support structures. Support structures are not always needed. Depending on the characteristics of the resin and length of the overhangs, short overhangs up to 3 cm angled 30° of the vertical usually do not need a support structure; this could range even up to the 45° of the vertical depending on the length of the overhang. Support structures, although necessary, increase the material cost, require postprocessing, and can cause damage to the object's surface in the removal process. Getting the 3D printing support structures right is therefore a very important aspect of 3D printing complicated models. In 3D printing processes that require support structure, orientation of the object has to be well-thought-out as it can significantly lower the need for the supports.

6.10 Advantages and disadvantages of vat photopolymerization processes

Besides vat photopolymerization there are also other AM processes based on different principles and using different materials. All of them have specific advantages and disadvantages which must be taken into consideration when choosing the appropriate technology for the specific task.

All the vat photopolymerization processes are relatively fast. Those working on the principle of mask projection show their advantages when printing large objects. Especially interesting in this respect are DLS systems enabling continuous production of the objects. The complexity of the objects produced by 3D printers is unparalleled by other

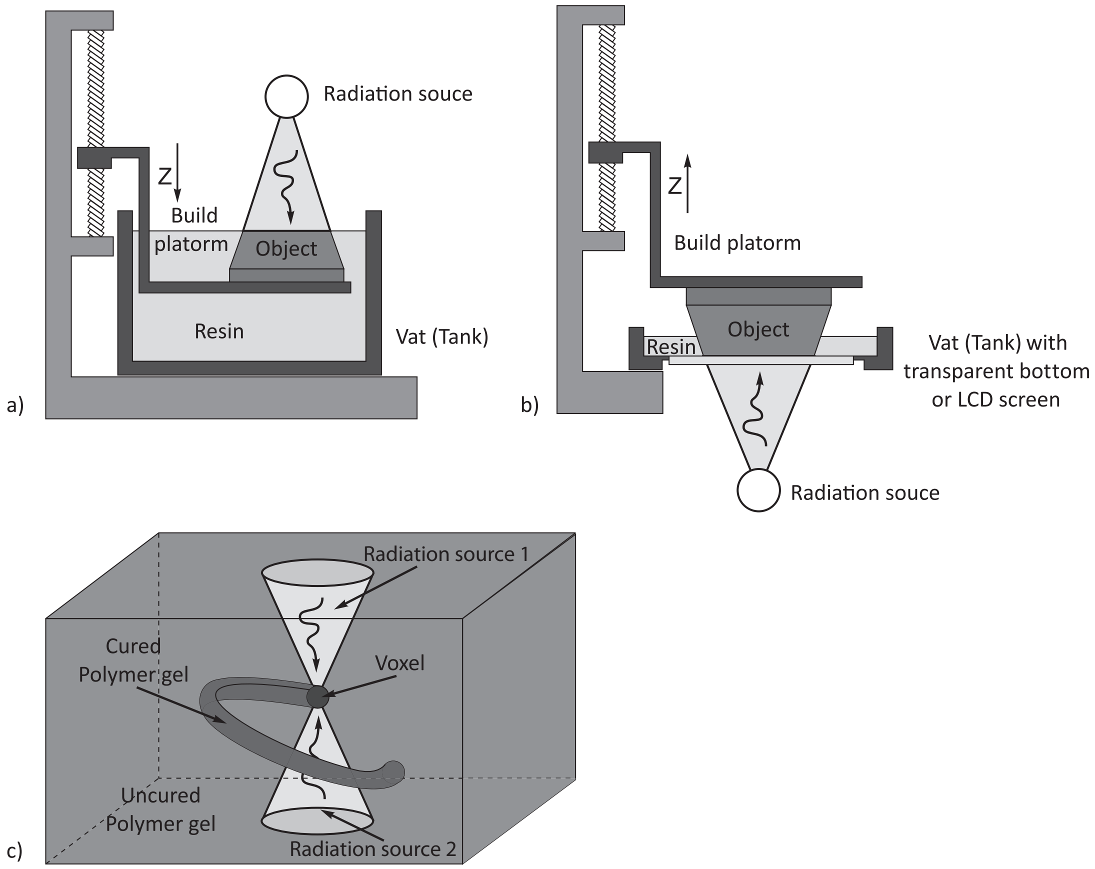

FIGURE 6.8 3D printer construction: (A) top-down approach, (B) bottom-up approach, (C) solidification in the volume of polymer gel block.

AM technologies, as the precision of this technology reaches production of details at the micrometer level. Objects have a highly isotropic structure, resulting in predictable mechanical performance critical for some applications. Watertightness is also one of the important characteristics for prototyping in some industries. Scalability of the process is simple where build volumes are reaching cubic meter, although fused deposition modeling (FDM) is the most scalable process of the AM process capable of building house sized objects. The resin that was not polymerized can be reused, so there is no wasted material. The versatility of resins that can be used to produce a soft or hard objects, resins can also be heavily filled with secondary materials like glass, ceramic, etc. thus producing different material characteristics. Vat photopolymerization is most suitable for biomedical molding application like dentistry and other high precision uses.

Disadvantages of the vat photopolymerization processes are tied to suitable materials, as they are limited to the photosensitive resin usage. Parts produced from these materials are often affected by moisture, light, heat, and chemicals. Mask projection processes cause stair-stepping instead of a smooth surface.

6.11 Applications of vat photopolymerization

AM technologies since their beginnings were embraced by the different industries, providing a platform for fast development of products accelerating prototyping and innovation. Engineering and product design in the automotive industry first embraced AM technologies. Vat photopolymerization with its advantages is often the process of choice to turn ideas into realistic proofs of concept, production of high-fidelity prototypes, production of custom tools, molds, and manufacturing aids. Besides prototyping these processes are being used also as main production technology. Jewelry design as a specific area of product design produces highly customized product fitted to the one person while using expensive materials benefits from fast prototyping with cheap material. Health care demands a highly individualized approach to orthopedics, implants, hearing aids, or production of medical devices and instruments. Dentistry almost solely uses vat photopolymerization due to its consistency, accuracy, and precision. Education relies on 3D printing in order to encourage creativity, especially interesting is the possibility to produce transparent objects revealing internal structures of otherwise opaque objects. The entertainment industry uses it for character design, sculpting, prop making, etc. Development of microstereolithography processes in the future will open new possibilities in the fields of photonic crystals, microelectronics, optoelectronics, and biological tissue printing. With decreasing prices of machines and polymer resins, increasing capabilities, availability and simplicity of use implementation of this technology is growing every day in all segments of the society.

6.12 Conclusion

Photopolymerization as the process of solidifying liquid resin under the influence of radiation offers diverse possibilities in the field of 3D printing. This is reflected in numerous approaches to the construction of the AM machines. Wide range of electromagnetic radiation sources, solutions for the selective radiation direction, and photopolymeric materials prove the vat photopolymerization as most diverse among all AM techniques. As the first invented principle of 3D printing, vat photopolymerization held up to date and it always competed with new technologies providing high precision of the objects, which is still an advantage over other 3D printing technologies available today. Variety of materials ensures precise definition of characteristics of the objects produced by this technology. Applicability in almost all industries reflects the versatility of the process. Shortcomings of vat photopolymerization come mainly from the restriction to photopolymeric materials which exclude production of functional metal parts. While MSLA shows promising potential in the manufacturing of microstructures, SLA, DLP, and LCD technologies are widely adopted by the industry as well as the hobby users.

References

[1] ISO/ASTM 52900:2015(en), Additive manufacturing — General principles — Terminology, International Organization for Standardization (ISO), Geneva, 2015.
[2] H.T. Black, M.C. Celina, J.R. McElhanon, Additive Manufacturing of Polymers: Materials Opportunities and Emerging Applications, Sandia National Laboratories, 2016.
[3] Y. Patil, R. Patil, N.S. Chnddrashekhar, K.P. Karunakaran, Layer separation mechanism in DLP 3D printing, in: Advances in Additive Manufacturing and Joining: Proceedings of AIMTDR, Springer, 2018, pp. 179—188.
[4] H. Gernsheim, A. Gernsheim, The History of Photography: From the Camera Obscura to the Beginning of the Modern Era, McGraw Hill, New York, NY, 1969.
[5] W. Terry, T. Gornet, History of Additive Manufacturing, Wohlers Report, 2016.
[6] W.K. Swainson, S.D. Kramer, Three-dimensional Pattern Making Methods, 1982. US Patent 4333165.
[7] W.K. Swainson, S.D. Kramer, Method and Media for Accessing Data in Three Dimensions, 1984. US Patent 4471470.
[8] H. Kodama, Automatic method for fabricating a three-dimensional plastic model with photohardening polymer, Rev. Sci. Instrum. 52 (1981) 1770—1773.
[9] A.J. Herbert, Solid object generation, J. Appl. Photogr. Eng. 8 (4) (1982) 185—188.
[10] A.J. Herbert, A review of 3D solid object generation, J. Imag. Technol. 15 (4) (August 1989) 186—190.
[11] C.W. Hull, Apparatus for Production of Three-Dimensional Objects by Stereolithography, 1986. US Patent 4575330.
[12] C.W. Hull, S.T. Spence, D.J. Albert, D.R. Smalley, R.A. Harlow, P. Steinbaugh, H.L. Tarnoff, H.D. Nguyen, C.W. Lewis, T.J. Vorgitch, D.Z. Remba, Method and Apparatus for Production of Three-Dimensional Objects by Stereolithography, 1991. US Patent 5059359.
[13] J.C. André, M. Cabrera, J.Y. Jezequel, A. Méhauté, Process for producing a model of an industrial component and device for implementing this process, 1985. French Patent 2,583,333.
[14] J.C. André, A. Méhauté, O. Witthe, Dispositif pour realiser un module de piece industrielle, 1984. French Pat. 8411241.
[15] L.J. Hornbeck, Spatial Light Modulator and Method, 1986. US Patent 4566935.
[16] A. Bertsch, H. Lorenz, P. Renaud, Combining microstereolithography and thick resist UV lithography for 3D microfabrication, in: 11th IEEE Workshop on Micro Electro Mechanical Systems (MEMS'98), 1998 (Heidelberg, Germany).
[17] T. Nakayama, Three-dimensional Model Manufacturing Device, 1991. Japan patent JPH03227222A.
[18] J.R. Tumbleston, et al., Continuous liquid interface production of 3D objects, Science 347 (2015) 1349—1351.
[19] L. Hornbeck, Digital Micromirror Device, 2009. US Patent No. 5,061,049, Inducted in.
[20] M.R. Douglass, Lifetime estimates and unique failure mechanisms of the Digital Micromirror Device (DMD), in: 1998 IEEE International Reliability Physics Symposium Proceedings 36th Annual (Cat No 98CH36173) RELPHY-98, 1998, ISBN 0-7803-4400-6, pp. 9—16, https://doi.org/10.1109/RELPHY.1998.670436.
[21] S. Maruo, S. Kawata, Two-photon-absorbed near-infrared photopolymerization for three-dimensional microfabrication, J. Microelectromech. Syst. 7 (4) (1998) 411—415.
[22] S. Maruo, O. Nakamura, S. Kawata, Three dimensional microfabrication with twophoton absorbed photopolymerization, in: SPIE — Optics for Science and New Technology, 1996.

CHAPTER

7

Material extrusion

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7.1 Method introduction

Technologies enabling the creation of three-dimensional objects are in constant and perpetual development. 3D printers are increasingly used in low volume production and the production of prototypes. Initially, they were used only for manufacturing of prototypes, now they are used in many areas for the production of i.a. parts and components [1]. Rapid prototyping methods are additive, which means that the model is built by applying the material layer by layer, which, depending on the technology, is subjected to sintering, melting, gluing, or curing with a laser [2]. Depending on the technology, the building material can be light-cured resin, thermoplastics, or polymer powders or even metal alloys.

The most popular 3D printing technologies include:

- Fused Filament Fabrication (FFF), the same technology as Fused Deposition Modeling (FDM),
- Selective Laser Sintering (SLS),
- Stereolithography (SLA),
- PolyJet Technology.

Taking into account the availability of devices and materials as well as the ease of use, the most common 3D printing technology is the FDM technology [3]. It was developed in 1989 by Scott Crump [1]. The principle of operation of machines using the FDM technology is shown in Fig. 7.1.

In this method, the material used to build the model is heated in the head to the melting temperature, then extruded through a nozzle and cooled again [4,5]. Thus, in the process of processing materials in the FDM technology, two phase changes occur under the influence of temperature changes—solid into plasticized and plasticized into solid [6]. Under ideal conditions, the head with extrusion nozzles controls the flow of material and moves in a thermally insulated working chamber [7]. The material is most often delivered to the extruder in the form of a filament (solid phase) [8], but some configurations also use granules and then the material is delivered through an appropriate funnel connected to the extruder [9].

In addition, FDM is a multi-object technology, which means that in one production process it is possible to produce many different spatial objects of which key parameters are defined in four main steps [10]:

1. Correct import of the STL file containing the model: checking the geometric correctness of the STL file; appropriate arrangement (orientation) of the model in the machine's working chamber;
2. Selection of basic parameters for the model: type of model material and/or type of support material, type of 3D printhead nozzles, height of a single layer of the model built, type of support, or support material used [21];
3. Selection of advanced model parameters: determination of the expected quality of external surfaces; determination of the method of filling the constructed model with material, for the FDM technique, selection of the appropriate internal geometry (type of filling used by Stratasys; Fig. 7.2) or in the case of the density level of the internal structure; determination of the method of paths execution (Fig. 7.3), the type of structure of the support material (Fig. 7.4) and related subparameters (Fig. 7.5).

Among the known additive techniques, only the FDM technique gives such extensive possibilities of preparing a model for printing [12]. One of the key and influential process parameters is the diameter of the nozzles forcing the

Polymers for 3D Printing
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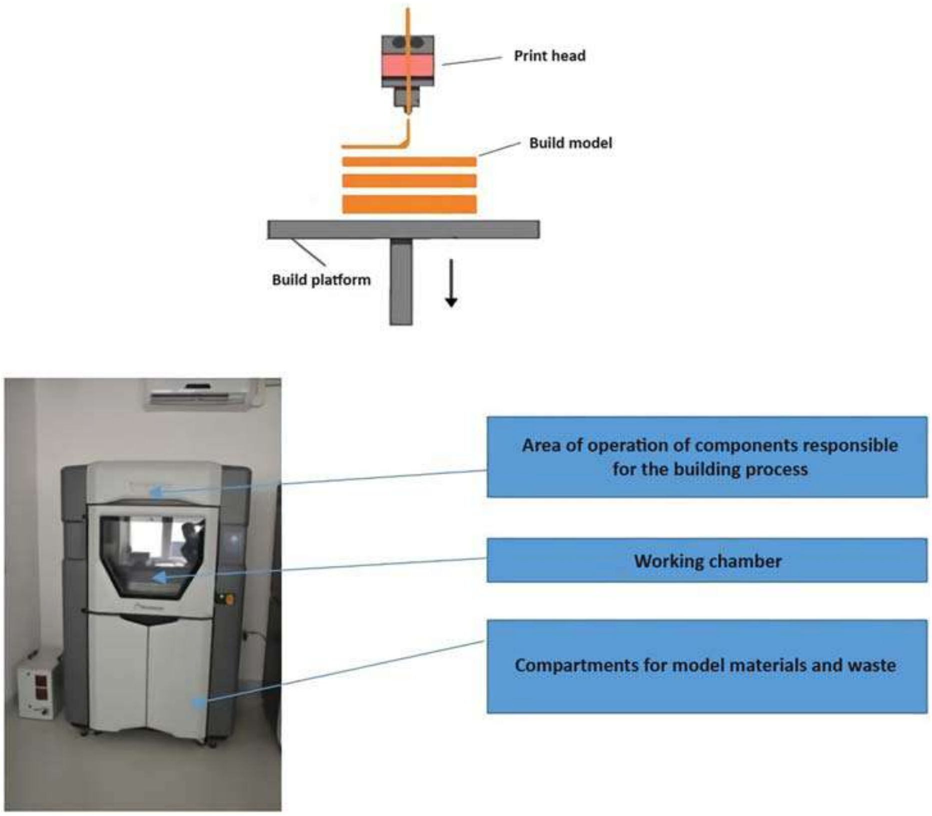
FIGURE 7.1 The principle of operation of the FDM method and division into three main modules present in every FDM machine.



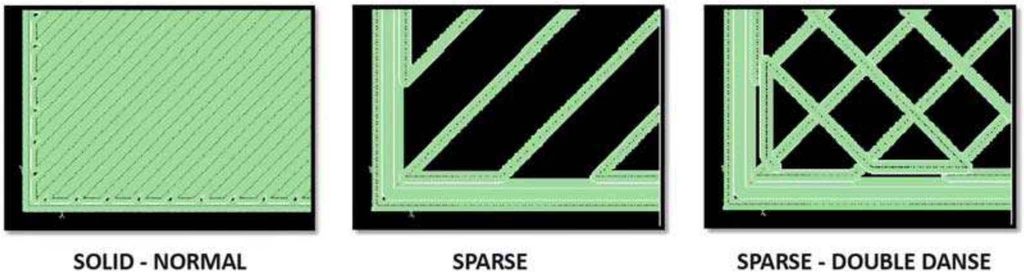


FIGURE 7.2 The figure shows examples of three factory-proposed fill geometries of the built model – solid–normal, sparse, and sparse–double dense [11].

materials. They are closely matched to the model material used, as shown in Table 7.1. This means that when choosing the material from which the model is to be made, the user has at his disposal one of the forcing nozzles dedicated to it, marked by one of the key manufacturers of FDM machines as: T10, T12, T16, and T20. These markings determine the height of a single layer of the model being built, and thus the time of building the model, which was presented in the examples.

Figs. 7.6–7.9 show examples illustrating the dependence of the model building time on the forcing nozzle used. Detailed data on the influence of the 3D printing main parameters on the process time and the strength of models, depending on the forcing nozzle used, are also presented.

In the above examples (Fig. 7.6), attention should be paid to a significant reduction in the production time of models depending on the injection nozzle used for the ABS-M30 material. Additionally, the decrease in consumption of the model material, which is related to the increase in the volume of the path diameter forced through the head, and thus the increase in the volume of air spaces between the layered paths, is clearly noticeable. The consumption of support material also changes, as it depends on the method of the applied path.

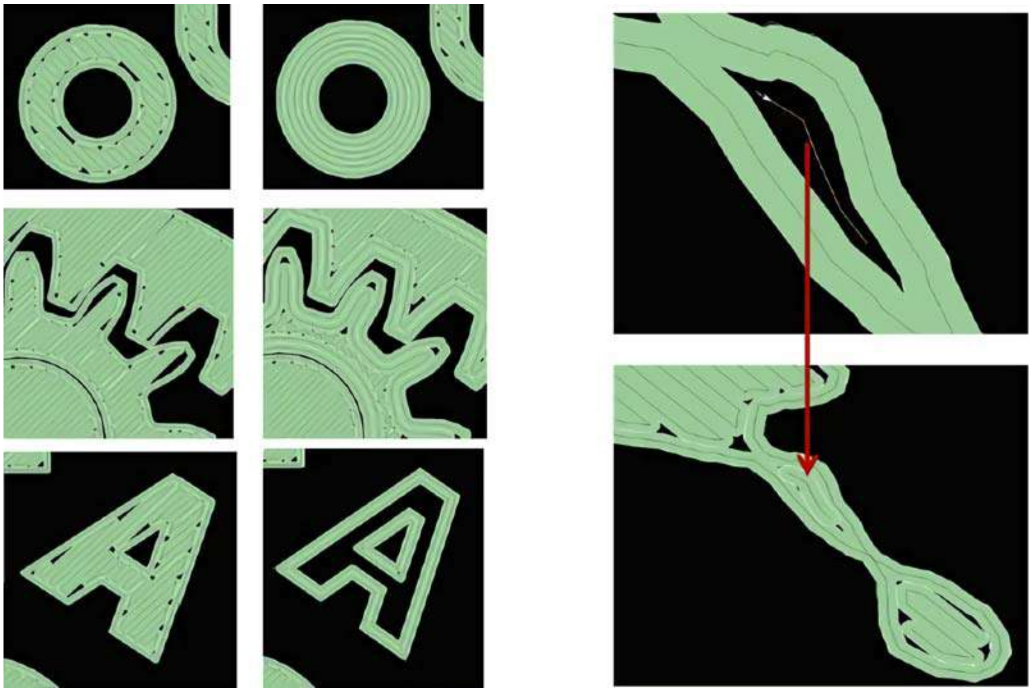
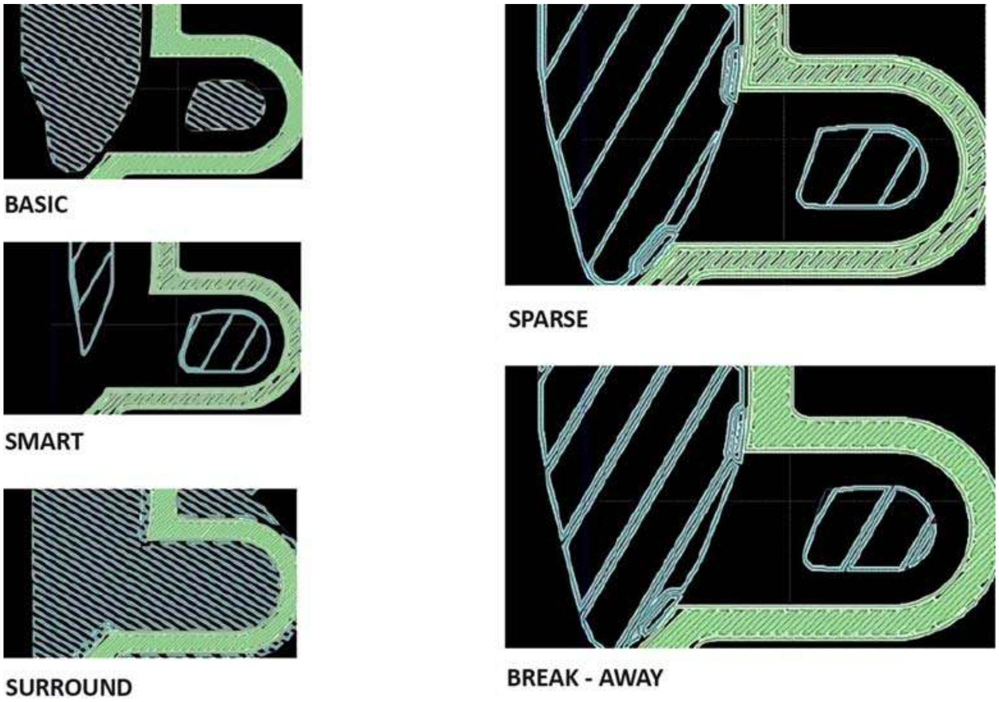


FIGURE 7.3 Examples of selected possibilities of programming the paths of the head applying materials in the FDM technique. The paths can be programmed automatically depending on the shape of the external model (example on the left) or independently of the shape—freely—by the operator (example on the right) [11].



BASIC

SMART

SURROUND

SPARSE

BREAK - AWAY

FIGURE 7.4 Cross section of a model built with the FDM method. The figure shows the four most representative ways of building support structures (blue), supporting the constructed object from a model material (green). *Examples prepared by Stratasys [11].*

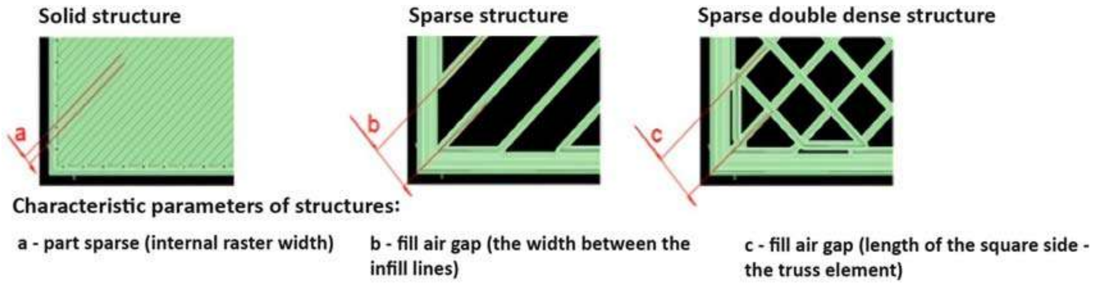


FIGURE 7.5 Representative subparameters that are responsible for programming the shape of the fill geometry of the built model [11].

TABLE 7.1 Table of correlation between forcing nozzles and selected materials used in the FDM technique.

Sample model material	Nozzle type supported, layer height value in parentheses
ABS-M30	T10 (0.127 mm) T12 (0.178 mm) T16 (0.254 mm) T20 (0.330 mm)
PC	T12 (0.178 mm) T16 (0.254 mm) T20 (0.330 mm)
ULTEM 9085	T16 (0.254 mm)

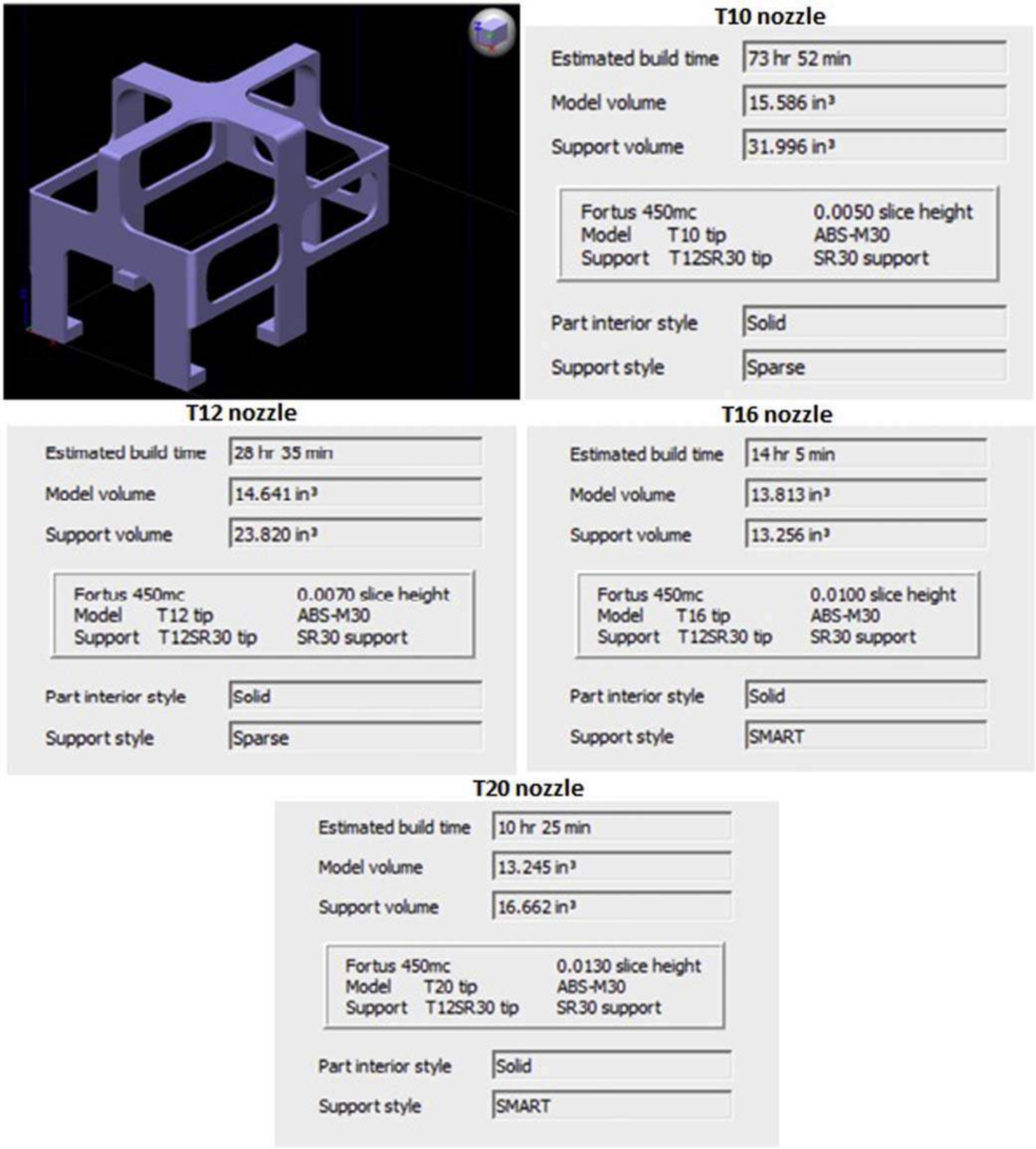
7.2 Machines/available equipment

The FDM technology is characterized by the general availability of devices operating in this technique. An additional advantage is the fact that there are many so-called open-source constructions—3D printers under the name Reprap. These are publicly available designs of self-replicating machines, i.e., those made of components and subassemblies that can be produced by the Reprap machines themselves and do not require their manufacturers to engage in maintenance activities. Their main advantage is cheap production, intuitive assembly, and the wide availability of parts and knowledge regarding the software and components. The initiator and manager of the Reprap project was Adrian Bowyer [13]. His design was based primarily on FDM technology and the results are released under the GNU license, which means that they are available for free and anyone can modify them for their own purposes [14]. These machines are characterized by a large number of parts made with the use of additive technologies and wide availability of software, control electronics, as well as electrical and electronic diagrams.

Depending on the design, there are single- and multi-head versions (most often two-head). The second printing head is designed to build support structures, which are most commonly printed from water-soluble material (BVOH, PVA) or suitable solvents (HIPS). Support structures are generated in places of the model where the model structure is not supported by previously created object paths or usually its walls inclination is greater than the angle of 45° (this does not apply to all types of materials for printing). A printer equipped with several printheads usually prints alternately (one extruder active, others at rest). In some types of printed devices, printing with several heads simultaneously is possible with the use of independently controlled heads (e.g., BCN3D Sigmax R19). The printing temperature range is as follows:

- head temperature: from 180°C to 300°C (some devices even up to 450°C),
- working platform temperature: up to 100°C,
- chamber temperature: up to 60°C (if available).

In order to print a three-dimensional object, the machine code should be properly prepared. It is created in specially designed programs (e.g., Simplify3D, Cura, MatterControl). A spatial object (usually STL) should be



T10 nozzle

Estimated build time 73 hr 52 min
Model volume 15.586 in³
Support volume 31.996 in³

Fortus 450mc 0.0050 slice height
Model T10 tip ABS-M30
Support T12SR30 tip SR30 support

Part interior style Solid
Support style Sparse

T12 nozzle

Estimated build time 28 hr 35 min
Model volume 14.641 in³
Support volume 23.820 in³

Fortus 450mc 0.0070 slice height
Model T12 tip ABS-M30
Support T12SR30 tip SR30 support

Part interior style Solid
Support style Sparse

T16 nozzle

Estimated build time 14 hr 5 min
Model volume 13.813 in³
Support volume 13.256 in³

Fortus 450mc 0.0100 slice height
Model T16 tip ABS-M30
Support T12SR30 tip SR30 support

Part interior style Solid
Support style SMART

T20 nozzle

Estimated build time 10 hr 25 min
Model volume 13.245 in³
Support volume 16.662 in³

Fortus 450mc 0.0130 slice height
Model T20 tip ABS-M30
Support T12SR30 tip SR30 support

Part interior style Solid
Support style SMART

FIGURE 7.6 Simulation of printing time of a rack model for electronics made with the use of a T10 nozzle, made of ABS-M30.

imported and then a number of parameters characterizing the future printout should be specified. The user is able to change i.a. the height of the print layer, the type and degree of model filling, printing speed, generation of special support structures, as well as temperatures of the heads and the build plate. A properly parameterized three-dimensional model is "cut" in the application and usually exported to a file with the GCODE extension.

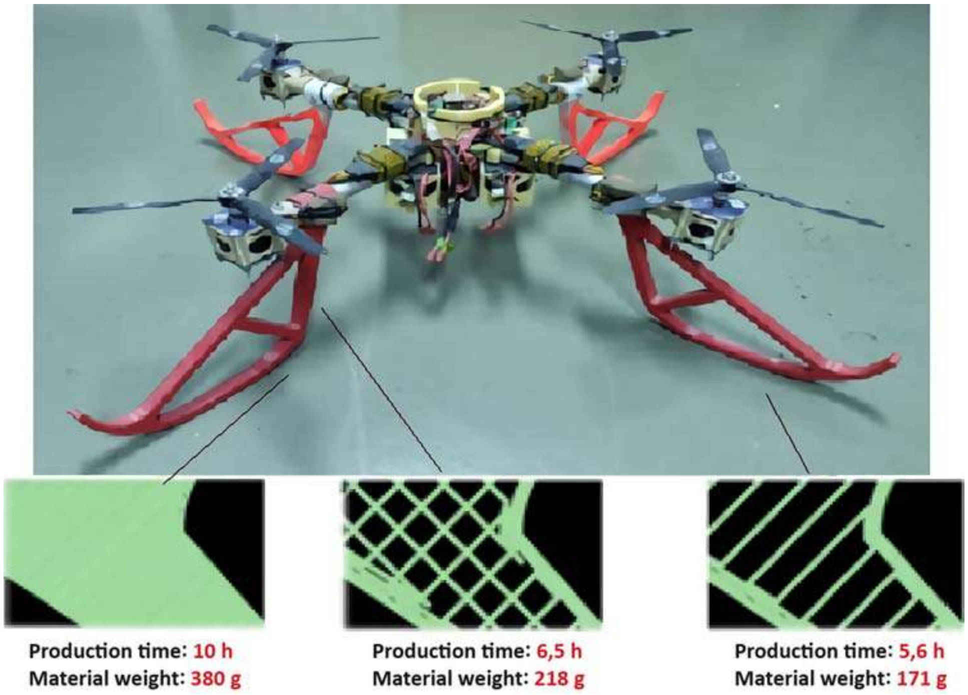


FIGURE 7.7 Simulation of the printing time of the model made of ABS-M30 material of the presented multirotor leg, using the T16 nozzle. The example shows the dependence of changes in the production time and material consumption for the model on the type of internal geometry used.

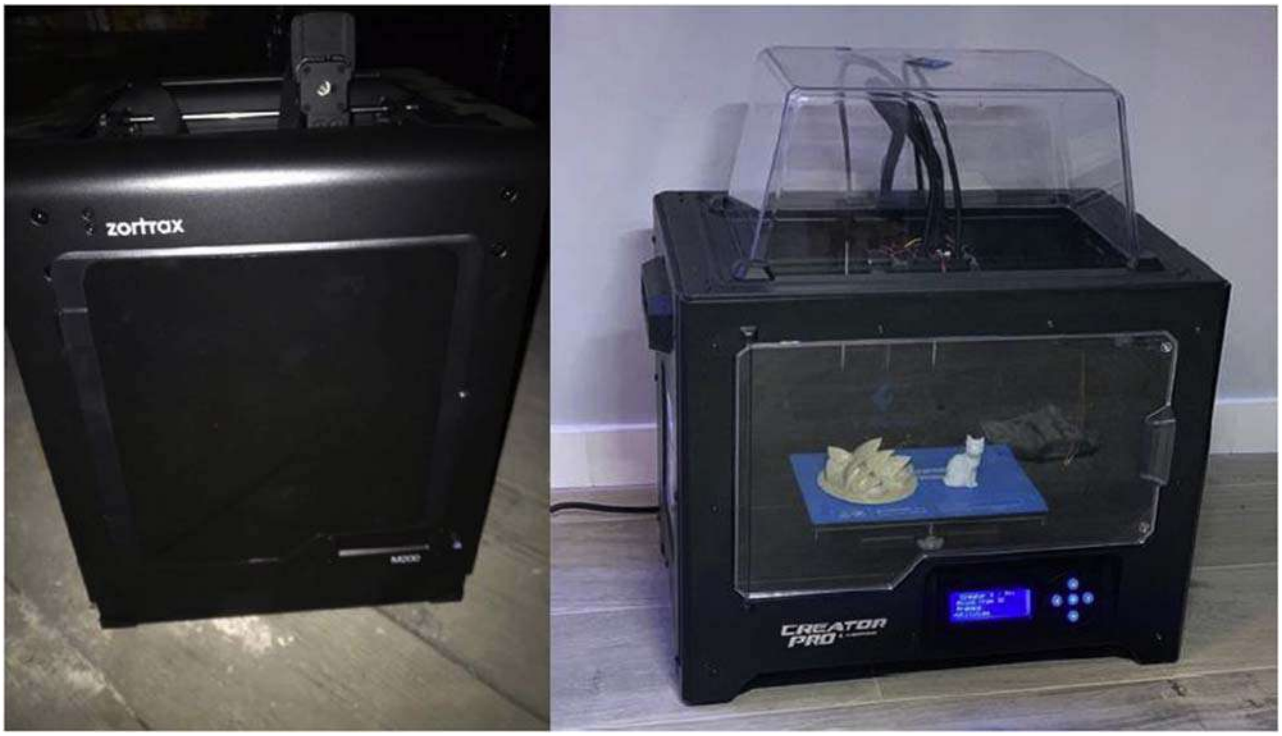


FIGURE 7.8 3D printers working in FDM technology.

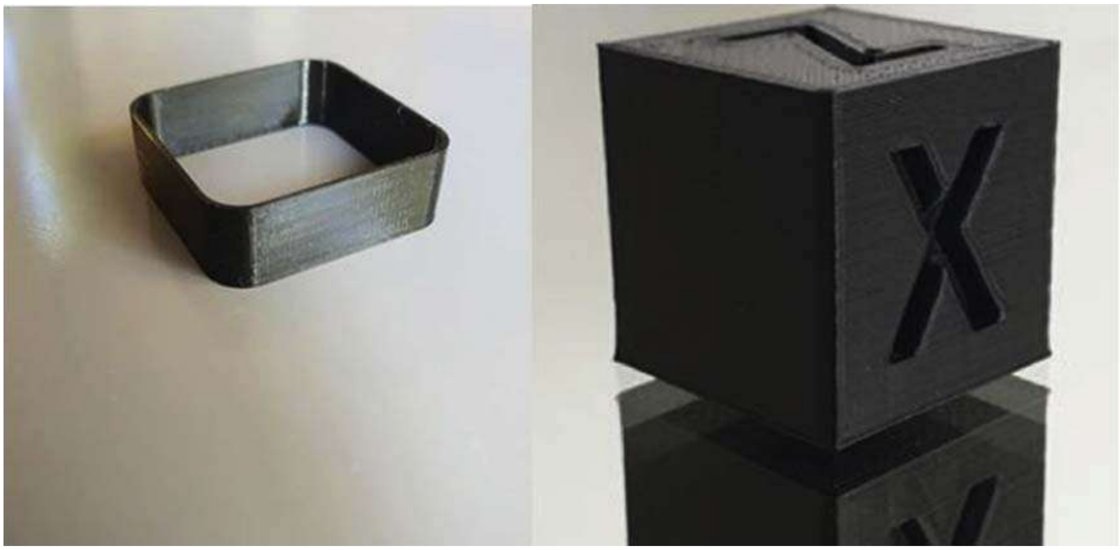


FIGURE 7.9 FDM printouts.

7.3 Polymers in material extrusion

Currently, the material base of FDM technology is very extensive. This technique supports all types of thermoplastic materials. These are plastics that change their viscosity and consistency after reaching the appropriate temperature. The FDM technology processes materials ranging from the most popular PLA (polylactide), PET (poly(ethylene terephthalate)), ABS (acrylonitrile-butadiene-styrene), to various types of technical nylons, polycarbonate (PC), and even high-temperature PEEK or ULTEM materials. An interesting fact is that the FDM technology allows printing from various types of elastomers (e.g., flex 40D) and mixed materials (e.g., PLA composites with carbon fiber).

The representative and most commonly used material in FDM technology is PLA. It is a material that can be processed by all classes of FDM/FFF machines. Table 7.2 describes its main properties. PLA can informally be considered as the base material for FDM technology. Its universality results mainly from the low shrinkage occurring as a result of the phase transformation of the plasticized material into the solid phase. PLA is a polymer that is obtained from renewable natural resources such as corn meal. It should be remembered that it is a biodegradable material [16]. Objects made of this raw material are characterized by high hardness and low impact strength. Due to its mechanical properties, this material is rarely used for manufacturing of structural and mechanical elements in production of machine parts. It is a material used for rapid prototyping and building production models focused on production planning using high-temperature materials. Fig. 7.9 shows exemplary PLA printouts.

TABLE 7.2 Technical specification of a representative Verbatim PLA material [15].

Diameter precision	**1.75 ± 0.03 [mm]**
Process Temp.	200–220°C
Melting Temp.	168°C
Density	1.24 g/cm^3
Glazing Temp.	58°C
Extensibility	63 Mpa
Elongation	4%
Melt flow rate (190°C, 21.2 N)	3.0 g (10 min)
Melt flow rate (210°C, 21.2 N)	8.1 g (10 min)

7.4 Software and executors file

In order to print a physical object its three-dimensional, digital representation – a CAD model—is needed. It can be created in appropriate parametric or nonparametric computer programs or by using a 3D scanner.

SketchUp, 3ds max, SolidWorks, or Inventor can be included among the generally available programs enabling modeling. The second method of obtaining the 3D geometry is 3D scanning. It is a process consisting in collecting a large number of point coordinates from a real object and recreating the surface of a spatial object on their basis. The surfaces are recreated on the basis of a point cloud, which is processed in dedicated software, where the points are combined into small triangular surfaces (polygons), and these into large surfaces reproducing the shape of the object with a specified accuracy.

The resulting polygonal model made of a mesh of triangles is a surface representation—a "shell" composed of n-polygons—which is saved to the appropriate file. The most commonly supported file format is STL. The mesh of polygons of the STL model based on triangles makes the mapping of arcs and circular elements of geometric objects somewhat simplified – burdened with a mapping error. This error can be reduced or increased consistently affecting the quality of the geometric representation of the object. This process is called tessellation and has a significant impact on the final form of a digital 3D object. The model prepared in this way should in the next stage undergo another process—generating an executive file that contains information about the required tool path—an extruder forcing the material – which is directly responsible for building the model. The representative runtime file is GCODE. It is a standardized command language that is used to operate numerically controlled (CNC) devices. It consists of a series of individual operations that, depending on the device, are able to create a detail by subtractive (e.g., CNC milling machines) or additive (3D printers) processing.

Currently, there are three known methods of generating executive files [15]:

- creating a list of commands in a text editor,
- code preparation using CAM software,
- entering commands directly through the device control panel.

Due to the time and ease of use, the executive files are generated in specially designed computer programs.

The generated three-dimensional object is imported in a computer program designed to prepare it for printing. Currently, there is a wide range of such applications, free and paid. This type of software includes a set of the most frequently used, among others, Slic3r, Cura, MatterControl, or Simplify3D.

A representative example is the Simplify3D slicer program, which is one of the paid programs. However, due to its ease of use and wide possibilities, it is very often chosen by users and constantly modified by communities and users. Based on the capabilities of this program, it is possible to select the main features of the FDM technology, the parameters of which are directly influenced by the user. Thus, the user has the possibility to changes in the height of the layer of the applied material—the printout, the type and degree of model filling—i.e., it may affect the shape and type of internal geometry of the filed object. The object produced in the FDM technology does not have to be solid inside, but it can have a freely programmed internal structure, e.g., honeycomb, truss, and ribs. In order to better illustrate the possibilities of the FDM technology and the model preparation process, Fig. 7.10 shows a representative software interface for FDM technology.

The program allows you to extract four main blocks consistent with the steps of preparing the geometric model and the batch file for the machine (GCODE):

1) Models: There are all imported 3D objects (with extensions STL, OBJ, and 3MF),
2) Visualization of the working area with the object/3D objects: The outline of the platform is visible along with the representation of the working chamber of the device. Additionally, the visualization shows the arrangement and orientation in space of objects that the user has prepared for printing,
3) Process window: Under the process name there are all settings of the printing process, including filling type and density or model layer height,
4) Menu: It contains a number of functions with which it is possible to change the orientation and position of three-dimensional objects and the definition of materials—i.e., machine parameters required in the processing of the indicated material. It allows also the direct communication with the printer and control of the process, mainly such parameters as: speed of the head movements and material extrusion, height of the model layer, printing temperature, type and degree of filling, and even cooling parameters of the material after its application.

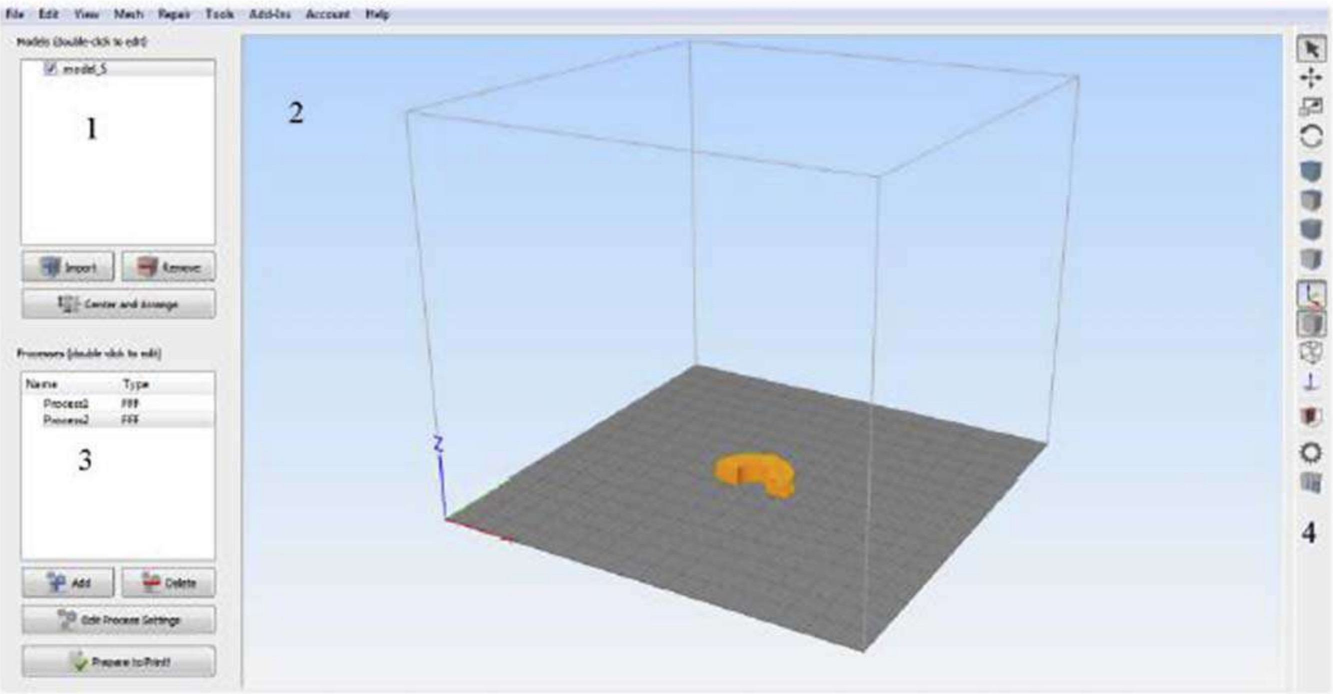


FIGURE 7.10 Interface of the Simplify3D program.

7.5 Postprocessing

Models produced in the FDM technology, as in the case of other additive methods, can be subjected to finishing treatment. The basic—main—stage of processing is the removal of support structures. They can be removed mechanically by breaking off or they can be dissolved [17]. In the second stage of treatment, the optional use of other additional methods of finishing allows the removal of the characteristic lines of joining the layers visible on the outer surfaces of the material, which in turn leads to a smooth and shiny surface of the printed object. Models produced in the FDM technology can be subjected to three types of treatment: mechanical, thermal, or chemical.

Mechanical processing consists in sanding the external surfaces of the model. For this purpose, sandpaper and small hand sanders are most often used. In order to polish the model, very small granulation sandpapers are used, which are additionally soaked in water.

Thermal processing of 3D printing is almost always associated with mechanical processing, with the use of heated tools. The heated tool facilitates the processing of 3D printed models, enabling use of much less force to shape the models than in, e.g., sanding or cutting off individual parts of a 3D print, as it is the case in mechanical processing. Thermal treatment is also used to improve the mechanical properties of specially prepared materials. An example is the PLA HD material by Fiberlogy, which improves its mechanical and strength properties after annealing.

Chemical treatment of 3D printing is most often used for materials based on ABS and other high-temperature polymers. Acetone or specially prepared alcohol (a mixture of ethanol and isopropanol) is the most frequently used substance for ABS, while for the PC (Polycarbonate) material, Dichloromethanol is used and for ULTEM materials, Trichloromethanol should be used. Chemical treatment most often consists in bathing the printed model in vapors of a solvent solution appropriate for a given model material.

In addition, the processing of printed models can be done using special resins with a hardener or plasticized with the use of a suitable solvent base material. This method consists in applying the resin or material on the external surfaces of the object with a brush or a blade acting as a putty knife. Fig. 7.11 shows the mechanical and chemical treatment of the printed models in the FDM technology.

7.6 Typical problems

FDM technology is not void of drawbacks. The main problems are related to generation of the correct GCODE file and the printing process itself. On the other hand, the selection of appropriate printing parameters is very important

FIGURE 7.11 3D printout after mechanical (*left*) and chemical (*right*) processing.

for the course of the process of producing the object model and unfortunately, at the very stage of preparation, a statistical user makes many mistakes related to setting the process parameters. The diagnosis is made on the basis of the defect analysis of the manufactured object and the group of the most common defects includes:

- the so-called "elephant feet": it is a slightly widened base of the printed object. Most often caused by too high temperature of the model table on which the object is built,
- warped edges of the printed object: caused by too much shrinkage of the material or too fast cooling of the object,
- losses between the walls and the filling of the object: most often the cause is incorrectly configured values of the width of the extruded material paths and the wrong choice of the diameter of the printing nozzle,
- filling of the model visible on the external walls of the model: the reason is a wrong setting related to the wall—too thin external wall,
- cracks on high objects: the reason is the lack of a heated printer chamber or too fast cooling of the model,
- misalignment of the applied layers: the reason is incorrect tension of the axle drive belts, slack in the kinematics system (Fig. 7.12D),
- losses in the layers of the model: too low printing temperature or the forcing nozzle partially clogged (Fig. 7.12C),
- poor reproduction of small details of the object: the reason is too high temperature of the head, too high speed of feeding the batch material to the head, or incorrectly selected speed of the fan cooling the printout during the printing process,
- visible undulation of the external surfaces of the object: caused by the wrong tension of the toothed belts of the printer's drive axes and inadequate acceleration of the head (Fig. 7.12B),
- cobweb effect: it is a wrongly set retraction of the print head, i.e., a parameter that is responsible for the retraction of the material at an appropriate speed over a given distance during idle head passes (Fig. 7.12A).

The following representative problems can be included in the group of issues related to the printing process itself:

- inadequate distance between the forcing nozzle and the surface of the printer model platform. Too large distance causes the printout to detach from the model table, while too small causes clogging of the head with the pressed material,
- no forcing of the material through the head: most often it is caused by the wrong selection of GCODE file parameters or poor quality of the printing material. In this case, poor material quality means uncontrolled admixtures in the structure of the base material, which accumulate during the forcing process and clog the nozzles,
- breakage of the material supplied to the head: most often it is caused by poor quality of the material or too much pressure of the base material in the extruder,
- insufficient adhesion of the printout to the surface of the model table: it is mainly caused by the selection of an inappropriate temperature of the surface of the table or not using an appropriate adhesive,

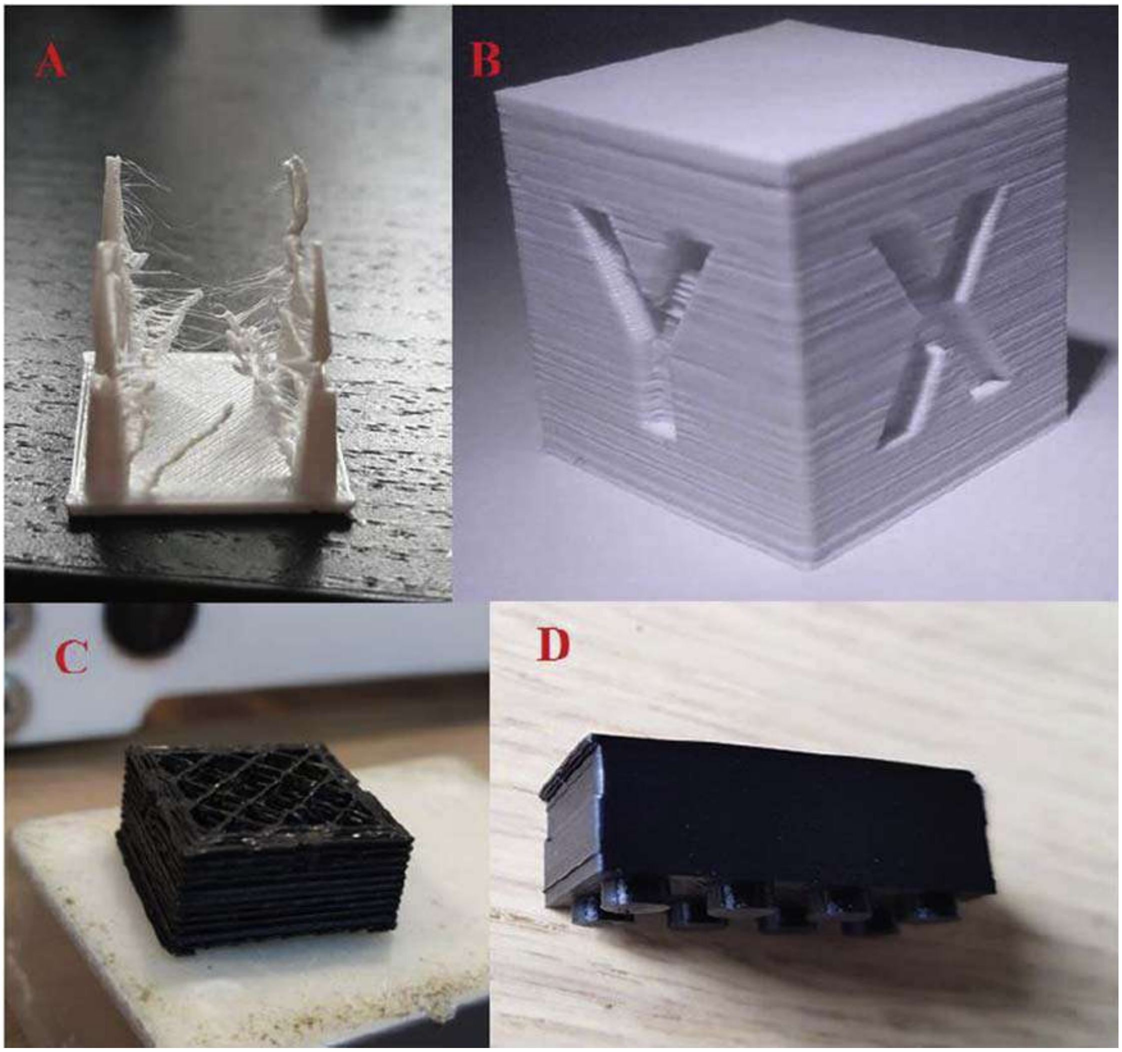


FIGURE 7.12 Examples of printing defects: (A) cobweb effect, (B) visible waving of the external surfaces of the model, (C) losses in the model layers, (D) shifts of the model layers.

- model shifts during printing: caused by the too high speed of key printer components responsible for building the object.

7.7 Advantages and disadvantages

The main advantages of FDM technology start with the low cost of the printer. Currently, prices start at around \$ 200. The FDM technology has become one of the most economical methods of producing thermoplastic elements, due to the fast rate of construction of parts and minimal material waste in relation to the volume of materials used for building models. These two features, combined with the possibility of printing elements from high-strength thermoplastics with high strength properties and high resistance to high temperatures and chemicals, as well as a wide selection of materials and relatively high accuracy of manufactured elements, have caused the FDM technology to take over 50% of the rapid prototyping market in the world. Other features of the FDM technology that are crucial in production are also important, e.g., the properties of materials intended for printing are similar to native plastics, despite the two-stage thermal treatment. What's more, the possibility of programming any configuration of the model being built—including filling density, height of the layer of the built object, thickness of the model walls—put FDM technology in the first place in terms of the possibility of programming the process and the number of model configuration parameters.

Unfortunately, despite its many advantages, FDM technology also has a number of significant disadvantages. The three main ones include, above all, high anisotropy of printed objects, relatively long time of manufacturing the objects, and the need to use support structures. Another disadvantage is the relatively low quality of the surface of the model, which is characterized by clearly visible and perceptible layers of the applied and hardened material. This entails the need for additional finishing treatment. All this, in turn, contributes to the relatively high cost of producing large objects in relation to other additive technologies, especially those that process plastics.

7.8 Technology applications

Despite the clear disadvantages of FDM, 3D printers working in this technology, due to their popularity, relatively low purchase and operating price, and a wide material base, have found widespread use in prototyping and low-series production [18] in many industries. Additive techniques are constantly and dynamically developing in various fields of industry and science, as shown in Fig. 7.13.

Similarly, the FDM technology is widely used in aviation, medical, or automotive industry, and even in architecture and construction. This is mainly due to the dynamic development of materials that receive certificates required by the indicated industries and due to the increasingly better fit of 3D printers to low-series and multifacility production. Production using FDM technology is becoming faster and repeatable [20].

7.9 Final considerations/concluding remarks and future insight

For FDM technology, as for any other 3D printing technology, the key is to make the optimal choice focused on the production parameters, which is made on the basis of at least a few main criteria:

1. The degree of complexity of the geometry intended for 3D printing,
2. The desired accuracy of 3D geometry,
3. Material requirements,
4. Strength requirements for the printed model,
5. Requirements for the internal structure and construction as well as external surfaces of the model,
6. The general purpose of the model.

With regard to the first and second criterion, it is very important to study the STL geometry relatively in detail in the context of the presence of geometric features of key importance from the point of view of 3D printing techniques. Considering 3 representative manufacturing technologies, 10 characteristic geometric features were identified that occur most often in STL models intended for 3D printing. In this context, the FDM technology was combined with two equally popular 3D printing technologies—SLS and PolyJET. The attached drawings were created based on

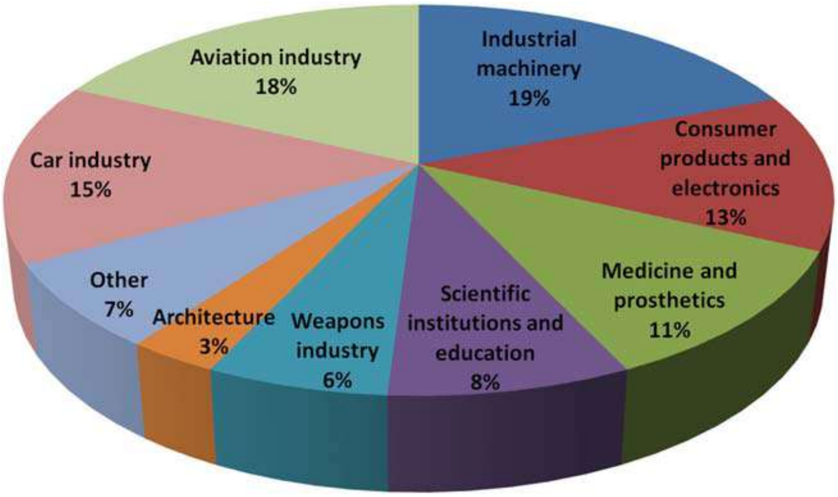


FIGURE 7.13 Percentage, statistical use of 3D printing in various branches of the economy and industry (Compiled on the basis of [19]).

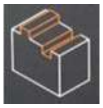
output of HUBS [22] and they reflect the ideas of the aforementioned geometric features very well. The FDM technology's suitability for production is assessed when review of the 3D model is focused on the analysis of the following geometric features:

1. Minimum thickness of supported walls—walls that are connected to the rest of the printout in at least two places.

   - for FDM technology: 0.8 mm,
   - for PolyJet technology: 0.5 mm,
   - for SLS technology: 0.7 mm.
2. Minimum thickness of unsupported walls—walls that are connected to the rest of the printout in less than two places.

   - for FDM technology: 0.8 mm,
   - for PolyJet technology: 1 mm,
   - for SLS technology: 0.7 mm.
3. Supports and overhangs—the maximum inclination angle of the walls of the printed model (relative to the model table) for which it is possible to print the model without supporting structures.

   - for FDM technology: 45°,
   - for PolyJet technology: support always required,
   - for SLS technology: not applicable.
4. Embossed and engraved primitives—minimal dimensions of primitives that are drawn (raised) or embedded below the surface of the model.



   - for FDM technology: height: 2 mm; width: 0.6 mm,
   - for PolyJet technology: height/width: 0.4 mm,
   - for SLS technology: height/width: 1 mm.
5. Bridges—the maximum length of model overhangs (bridges) that can be printed without supporting structure.

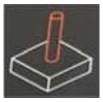
   - for FDM technology: height: 10 mm,
   - for PolyJet technology: support always required,
   - for SLS technology: not applicable.

6. Holes—the minimum diameter of the holes to be printed in the tolerance declared for the machine.

   - for FDM technology: ∅ 2 mm,
   - for PolyJet technology: ∅ 0.5 mm,
   - for SLS technology: ∅ 1.5 mm.
7. Connections—recommended clearances between two mating or moving (sliding/basic connection) parts.

   - for FDM technology: 0.5 mm,
   - for PolyJet technology: 0.2 mm,
   - for SLS technology: parts moving relative to each other 0.3 mm; mating parts 0.1 mm,
8. The minimum dimension of a primitive—the minimum dimension of any primitive for which the method of creation (3D printing/technology) does not introduce distortions.

   - for FDM technology: 2 mm,
   - for PolyJet technology: 0.2 mm,
   - for SLS technology: 0.8 mm.
9. Minimum pin size—minimum pin diameter for which the method of creation (3D printing/technology) does not introduce distortions.



   - for FDM technology: ∅ 3 mm,
   - for PolyJet technology: ∅ 0.5 mm,
   - for SLS technology: ∅ 0.8 mm.
10. Expected tolerance—technology dimensional accuracy

   - for FDM technology: ∓0.5% (lower limit ∓0.5 mm),
   - for PolyJet technology: ∓0.5% (lower limit ∓0.15 mm),
   - for SLS technology: ∓0.3% (lower limit ∓0.5 mm).

In the context of the third and fourth criteria, it is very important to make a relatively detailed comparative analysis in terms of parameters and material properties of processed structures, i.e., the base material that has been processed in the FDM process.

References

[1] K. Chou, Y. Zhang, A parametric study of part distortion in fused deposition modeling using three dimensional element analysis, Proc. Inst. Mech. Eng. Part B J. Eng. Manuf. Part B 222 (2008) 959—967.

[2] M. Srivastava, S. Maheshwari, T.K. Kundra, Virtual modelling and simulation of functionally graded material component using FDM technique, Mater. Today Proc. 2 (2015) 3471—3480.

[3] R. Singh, S. Singh, Development of nylon based FDM filament for rapid tooling application, J. Inst. Eng. India Ser. C 95 (2014) 103—108.

[4] K. Sood Anoop, A. Equbal, Metallization on FDM processed parts using electroless procedure, Procedia Mater. Sci. 6 (2014) 1197—1206.

[5] K. Sood Anoop, R.K. Ohdar, S.S. Mahapatra, Experimental investigation and empirical modelling of FDM process for compressive strength improvement, J. Adv. Res. 3 (2012) 81—90.

[6] T. Galeta, P. Raos, M. Somolanji, Impact of structure and building orientation onstrength of 3D printed models, KGK — Kautsch. Gummi Kunstst. 65 (10) (2012) 36—42.

[7] K. Sood Anoop, R.K. Ohdar, S.S. Mahapatra, Improving dimensional accuracy of fused deposition modelling processed part using grey Taguchi metod, Mater. Des. 30 (2009) 4243—4252.

[8] K. Sood Anoop, R.K. Ohdar, S.S. Mahapatra, Parametric appraisal of mechanical property of fused deposition modelling processed parts, Mater. Des. 31 (2010) 287—295.

[9] S. Christ, M. Schnabel, E. Vorndran, J. Groll, U. Gbureck, Fiber reinforcement during 3D printing, Mater. Lett. 139 (2015) 165—168.

[10] K. Sood Anoop, V. Chaturvedi, S. Datta, S.S. Mahapatra, Optimization of process parameter in fused deposition modeling using weighted principle component analysis, J. Adv. Manuf. Syst. 10 (2) (2011) 241—250.

[11] M. Cader, M. Uszyńska, Analiza zależności czasu budowania modeli od zmian parametrów wytwarzania w technologii FDM (Analysis of dependence between models building time and changes of parameters of fused deposition modeling FDM), Mechanik 86 (2013).

[12] K. Sood Anoop, E. Asif, V. Toppo, R.K. Ohdar, S.S. Mahapatra, An investigation on sliding wear of FDM built parts, CIRP J. Manuf. Sci. Technol. 5 (2012) 48—54.

[13] D. Croccolo, M. De Agostinis, G. Olmi, Experimental characterization and analytical modelling of the mechanical behaviour of fused deposition processed parts made of ABS-M30, Comput. Mater. Sci. 79 (2013) 506—518.

[14] M. Cygnar, P. Woś, G. Budzik, Analiza numeryczna i fizyczna modelu wykonanego przyrostową metodą FDM, in: Materiały konferencyjne I Krajowej Konferencji Naukowej Szybkie prototypowanie: Modelowanie-Wytwarzanie-Pomiary, 16—18 września, 2015, pp. 35—39. Rzeszów—Pstrągowa.

[15] A. Daekeon, J.-H. Kweon, S. Kwon, J. Song, S. Lee, Representation of surface roughness in fused deposition modelling, J. Mater. Process. Technol. 209 (2009) 5593—5600.

[16] H. Czyż, G. Budzik, R. Bienkiewicz, Wybrane aspekty szybkiego prototypowania modeli do zastosowań w inżynierii medycznej, in: Materiały konferencyjne I Krajowej Konferencji Naukowej Szybkie prototypowanie: Modelowanie-Wytwarzanie-Pomiary, 16—18 września, 2015, pp. 40—45. Rzeszów—Pstrągowa.

[17] T. Dani, P. Kamdi, G. Nalamwar, V. Borse, Multi objective optimization of built orientation for rapid prototyping of connecting rod, Int. J. Sci. Res. Manag. 1 (1) (2013) 13—18.

[18] M. Domingo-Espin, M. Puigoriol-Forcada Josep, G.-G. Andres-Amador, J. Llumà, B. Salvador, R. Guillermo, Mechanical property characterization and simulationoffused deposition modeling Polycarbonate parts, Mater. Des. 83 (2015) 670—677.

[19] M. Cader, Dobór geometrii wypełnienia prototypów wytwarzanych przyrostowo z polimeru ABSM30 (Selection of filling geometry of additive manufactured prototypes made of ABSM30 polymer), in: PhD Thesis, Rzeszów University of Technology, 2016.

[20] C. Tosto, A. Latteri, E. Pergolizzi, D. Giordano, G. Abramo, R. Catenaro, N. Pignotti, G. Cicala, Additive manufacturing of plastics: an efficient approach for composite tooling, Macromol. Symp. 389 (1) (2020).

[21] L.M. Galantucci, F. Lavecchia, G. Percoco, Study of compression properties of topologically optimized FDM made structured parts, CIRP Ann. Manuf. Technol. 57 (2008) 243—246.

[22] HUBS. Knowledge base. https://www.hubs.com/knowledge-base/. (Accessed 12 July 2020).

C H A P T E R

8

Material jetting

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8.1 Multi jet printing – description of technology

Multi Jet Printing known also as Multi Jet Modeling – MJP—is one of 3D printing technology using inkjet print heads [1]. It was launched in 1996 [2]. This technology is multicolor with UV-curable resin, without powder beds. This is the reason why MJP creates stronger parts. The process is easy and fast because washing away of material is simple and doesn't damage the product. Where necessary, printers additionally produce a gel support material which can be easily removed [1].

MJP technology is used to create durable components in high definition and in a short time. The prints are made of wax; this is the reason why postprinting is a simple and quick process. 3D printers working in Multi Jet technology are user-friendly, adapted to office needs, and can be operated remotely. However, the prints have poor mechanical strength compared to, for example, SLS technology; hence it is recommended to use MJP primarily in prototyping, and not in functional prints [3].

The principle of MJP is layering in three dimensions (Figs. 8.1 and 8.2). Inkjet head goes to and back to make one layer in *X*-axis, than in *Y*-axis. During printing, UV lamps cure photopolymers. The last layer in *Z*-axis is created by distancing platform from inkjet head. The process is repeated till the whole prototype is ready [2,4].

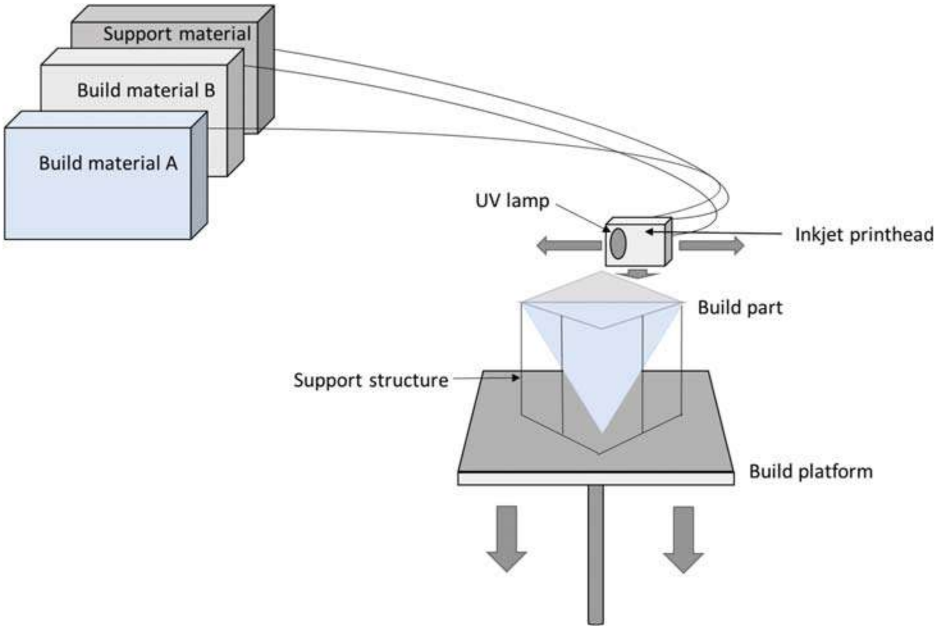


FIGURE 8.1 The principle of multi jet printing.

https://doi.org/10.1016/B978-0-12-818311-3.00022-7

FIGURE 8.2 The principle of Multi Jet Modeling.

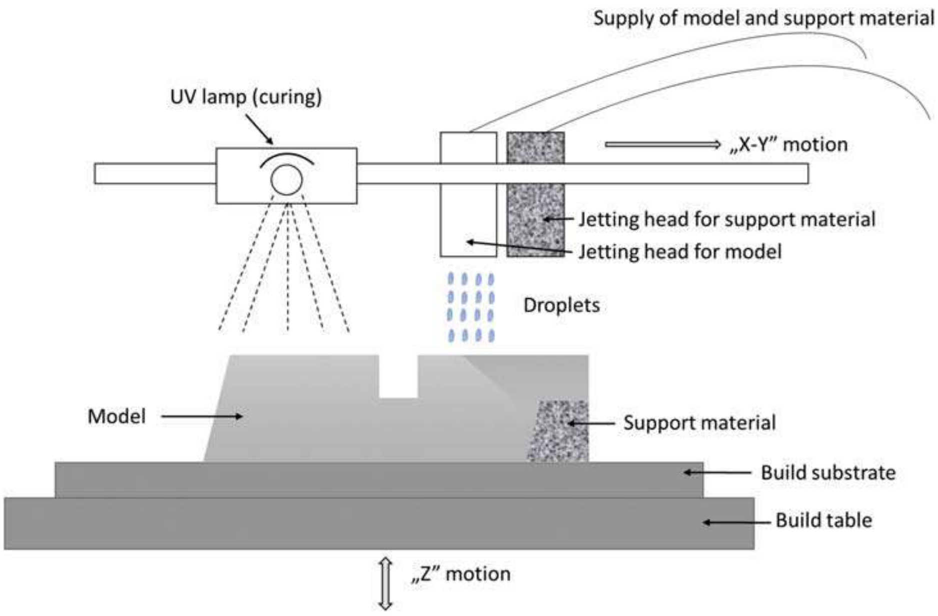


FIGURE 8.3 Actua 2100 [5].

The first MJP machine was Actua 2100 produced by 3D Systems company, existing till today (Fig. 8.3). It has size of medium digital printing machine or photocopier. It can be connected to the office network and receive jobs via internet. The Multi Jet head has 96 nozzles (4 rows per 24). The removal process is very simple – it can be done by hand [6].

3D printing technology is successfully used in medicine. It has application in organ printing, disease model developing, unusual dose of pharmaceutical products manufacturing, and cells bioprinting [7]. Multi Jet method is utilized in medicine, especially in dental.

3D Systems produces ProJet Series for plastics. Producer claims its machines can print with CAD accuracy. It is two times faster than other similar printers. Products are heat resistant, durable, watertight, and biocompatible.

8.1.1 *ProJet 3600*

ProJet 3600 (Fig. 8.4) is dedicated to elastomeric or plastic prototypes. Built models are robust and finished clearly. Machines can be used 24 h per 7 days a week. ProJet 3600 Dental (Fig. 8.5) produces, i.e., teeth in detail resolution. It's very important for patients because they can be sure dental products will be prepared properly without need for remakes. Process of production is faster and more economic than in other (not 3D) methods of making teeth.

FIGURE 8.4 ProJet MJP 3600 [5].

FIGURE 8.5 ProJet MJP 3600 dental [5].

8.1.2 *ProJet MJP 5600*

ProJet MJP 5600 (see: Fig. 8.6) is dedicated to products made of multiple materials, like rigid or flexible photopolymers. The materials can be white, gray, black. Their surface is very smooth and edges are sharp. Production is made layer by layer. Products created by ProJet are used in, i.e., manufacturing industry and medicine; they have varying degrees of material transparency and flexibility; shades can also be different. MJP 5600 works two times faster than similar printers. It can produce elements 0.5 m long or several smaller in one production cycle.

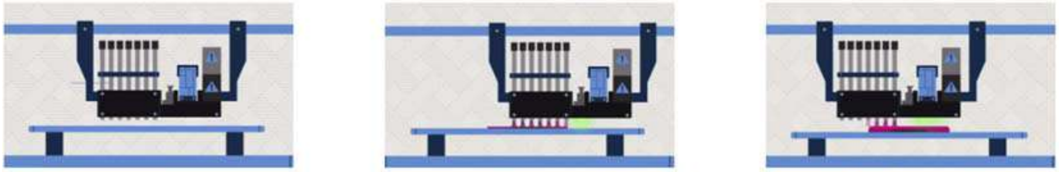
8.2 PolyJet modeling — description of technology

PolyJet Modeling is very similar to inkjet printing but machines instead of ink are jetting liquid plastic which is cured by UV light (Figs. 8.7 and 8.8). After curing, liquid is solidified. This process which is also used in SLA technology is called photopolymerization. Patterns are formed layer by layer; they are smooth, multicolor, and detailed. Another advantage is the ability to build models from a wide range of hard (ABS-like), flexible (rubber-like), and transparent materials. Layer resolution can achieve 0.014 mm. To support complicated geometries, gel-like support material is used. It can be removed by water jetting or by hand easily [9,10].

PolyJet Modeling is similar to MJP. It was invented by Stratasys — company which was started in 1989. It is the first technology to dispense two types of resins simultaneously in a single 3D printing process. It offers the unique ability to print multimaterial parts and components with different mechanical or physical properties — all in one process.

Today Stratasys produces different kind of 3D printing machines. PolyJet series are: Connex1, Connex3, J700 Dental, Objet30.

FIGURE 8.6 ProJet MJP 5600 [5].



PolyJet printer getting ready

Tiny droplets of photopolymers are deposited in the workspace through a carriage

Materials solidify when exposed to UV light, and process continues until a complete 3D object is formed

FIGURE 8.7 Stages of PolyJet modeling [8].

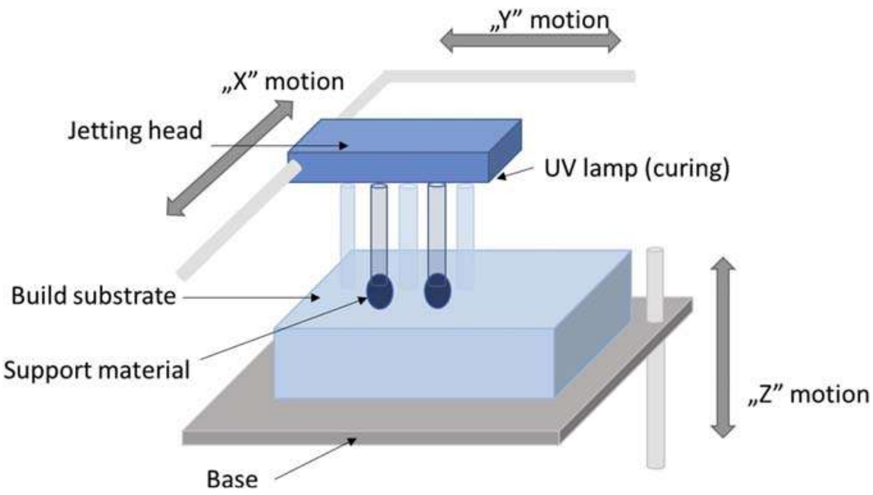


FIGURE 8.8 Principle of PolyJet modeling.

FIGURE 8.9 Connex1 Objet500 [8].

8.2.1 Connex1 Objet500

In this machine (Fig. 8.9) can be used 17 types of resins like rubber, plastics, polypropylene, and more. Patterns are created directly from CAD file—the process is very simple, fast, and accurate [8].

8.2.2 Connex3 Objet250, Objet500

These models (Objet500 is presented in Fig. 8.10) create opaque and transparent products; they can also be biocompatible and resistant to high temperature. Thanks to Connex3 precision, production is very fast and patterns are accurate. They can be multicolor or in three color gradients [8].

FIGURE 8.10 Connex3 Objet500 [8].

FIGURE 8.11 J700 dental [8].

8.2.3 *J700 dental*

J Dental series machines for dental industry are fast and they print with multiple materials. Created models of teeth are accurate in size and color according to original patient's mouth. J700 series (Fig. 8.11) are almost two times faster than SLA (stereolithographic) and DLP (digital light processing) printers [8].

There are research studies concluding PolyJet Modeling assures higher accuracy in making teeth than traditional (not 3D) technologies. The researchers at the Department of Orthodontics of Wonkwang University Dental Hospital, South Korea, prepared original teeth and scanned them to form 3D structures. They formed new teeth in two technologies – FDM (fused deposition modeling) and PolyJet. The surface of FDM model was more rough than the PM model (Fig. 8.12). However, both technologies gave clinically acceptable results [8].

8.2.4 *Objet30*

This machine is used for medical industry. It uses material which will be in prolonged skin contact. Objet30 is able to create ears and surgical elements (Fig. 8.13).

FIGURE 8.12 Original tooth, FDM model, PM model [9].

FIGURE 8.13 Objet30 [8].

8.3 Materials

8.3.1 *MJP materials*

In MJP technology there can be used various materials such as composite, plastic, and dental.

8.3.1.1 Composite

As well as printing in pure base materials, MJP machines can precisely mix any two base materials together, to achieve better mechanical properties and custom performance features in up to 12 different composite ratios. A whole object can be printed in any of these composites, or a user is able to simply choose a specific fragment of a part to be any number of different material combinations.

8.3.1.2 Plastic

In this category there are: polypropylene-like materials, ABS-like materials, nylon, biocompatible, elastomeric, and transparent materials.

In medical and nonmedical application VisiJet can be used in five different versions (Fig. 8.14). It exists in four colors (opaque black, opaque white, translucent clear, and natural). VisiJet CR models have different tensile strength, tensile modulus, elongation break, and impact strength. What is more, their heat distortion temperature isn't also similar. Only their water absorption has the same value. However, when it comes to models VisiJet CE, all parameters are the same [5].

8.3.1.3 Dental

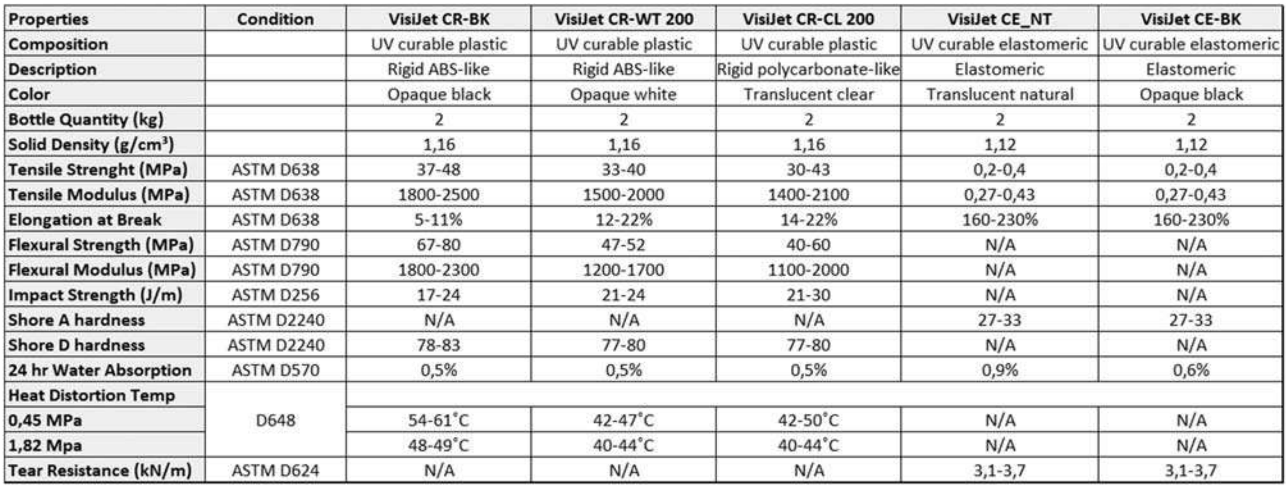
Materials used for dental purpose are translucent or with solid stone appearance. VisiJet M3 Stoneplast is useful for dentist and dental labs. It can be utilized in jaw models, orthodontic structures, etc.

For orthodontic models, implants, and crowns, VisiJet M3 Pearlstone is the most appropriate. VisiJet M3 Dentcast can be used in bridges, crowns, and prosthesis. It has dark green color and smooth surface.

Parameters of presented dental materials are mentioned in table (Fig. 8.15). The greatest differences in values are for tensile strength, tensile modulus, elongation at break, and heat distortion temperature [5].

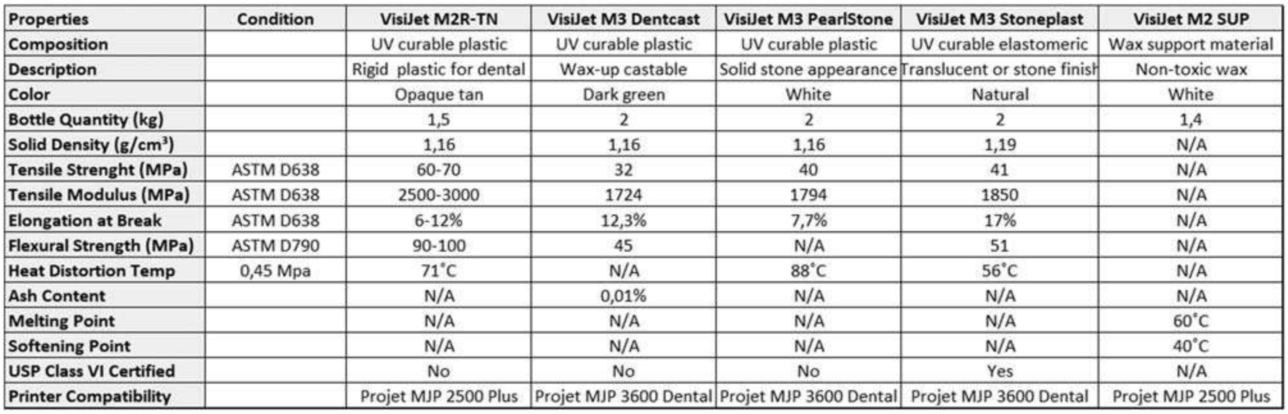
8.3.2 *PJ materials*

There are various types of PolyJet photopolymers, connected with their destination. Agilus30 has superior tear resistance, capable of resist bending and repeated flexing. It is very good material for rapid prototyping and design validation; this rubber-like material simulates the role, appearance, sense of rubber-like products (Fig. 8.16). Agilus30 is available in two colors — black or white. The black one has higher tensile strength and elongation at break. However, compressive set and tensile tear resistance are the same for the white and for the black one [8].



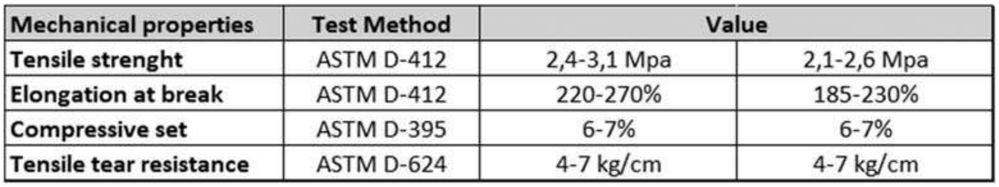
Properties	Condition	VisiJet CR-BK	VisiJet CR-WT 200	VisiJet CR-CL 200	VisiJet CE_NT	VisiJet CE-BK
Composition		UV curable plastic	UV curable plastic	UV curable plastic	UV curable elastomeric	UV curable elastomeric
Description		Rigid ABS-like	Rigid ABS-like	Rigid polycarbonate-like	Elastomeric	Elastomeric
Color		Opaque black	Opaque white	Translucent clear	Translucent natural	Opaque black
Bottle Quantity (kg)		2	2	2	2	2
Solid Density (g/cm³)		1,16	1,16	1,16	1,12	1,12
Tensile Strenght (MPa)	ASTM D638	37-48	33-40	30-43	0,2-0,4	0,2-0,4
Tensile Modulus (MPa)	ASTM D638	1800-2500	1500-2000	1400-2100	0,27-0,43	0,27-0,43
Elongation at Break	ASTM D638	5-11%	12-22%	14-22%	160-230%	160-230%
Flexural Strength (MPa)	ASTM D790	67-80	47-52	40-60	N/A	N/A
Flexural Modulus (MPa)	ASTM D790	1800-2300	1200-1700	1100-2000	N/A	N/A
Impact Strength (J/m)	ASTM D256	17-24	21-24	21-30	N/A	N/A
Shore A hardness	ASTM D2240	N/A	N/A	N/A	27-33	27-33
Shore D hardness	ASTM D2240	78-83	77-80	77-80	N/A	N/A
24 hr Water Absorption	ASTM D570	0,5%	0,5%	0,5%	0,9%	0,6%
Heat Distortion Temp	D648					
0,45 MPa		54-61°C	42-47°C	42-50°C	N/A	N/A
1,82 Mpa		48-49°C	40-44°C	40-44°C	N/A	N/A
Tear Resistance (kN/m)	ASTM D624	N/A	N/A	N/A	3,1-3,7	3,1-3,7

FIGURE 8.14 Plastic and elastomeric materials data sheet.



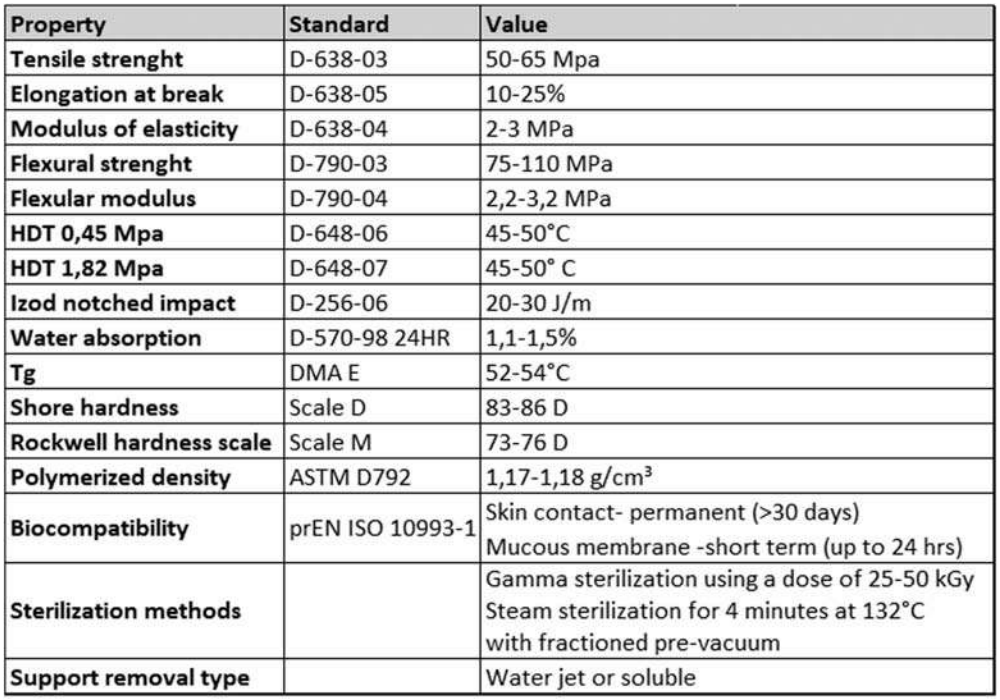
Properties	Condition	VisiJet M2R-TN	VisiJet M3 Dentcast	VisiJet M3 PearlStone	VisiJet M3 Stoneplast	VisiJet M2 SUP
Composition		UV curable plastic	UV curable plastic	UV curable plastic	UV curable elastomeric	Wax support material
Description		Rigid plastic for dental	Wax-up castable	Solid stone appearance	Translucent or stone finish	Non-toxic wax
Color		Opaque tan	Dark green	White	Natural	White
Bottle Quantity (kg)		1,5	2	2	2	1,4
Solid Density (g/cm³)		1,16	1,16	1,16	1,19	N/A
Tensile Strenght (MPa)	ASTM D638	60-70	32	40	41	N/A
Tensile Modulus (MPa)	ASTM D638	2500-3000	1724	1794	1850	N/A
Elongation at Break	ASTM D638	6-12%	12,3%	7,7%	17%	N/A
Flexural Strength (MPa)	ASTM D790	90-100	45	N/A	51	N/A
Heat Distortion Temp	0,45 Mpa	71°C	N/A	88°C	56°C	N/A
Ash Content		N/A	0,01%	N/A	N/A	N/A
Melting Point		N/A	N/A	N/A	N/A	60°C
Softening Point		N/A	N/A	N/A	N/A	40°C
USP Class VI Certified		No	No	No	Yes	N/A
Printer Compatibility		Projet MJP 2500 Plus	Projet MJP 3600 Dental	Projet MJP 3600 Dental	Projet MJP 3600 Dental	Projet MJP 2500 Plus

FIGURE 8.15 Dental materials data sheet.



Mechanical properties	Test Method	Value	
Tensile strenght	ASTM D-412	2,4-3,1 Mpa	2,1-2,6 Mpa
Elongation at break	ASTM D-412	220-270%	185-230%
Compressive set	ASTM D-395	6-7%	6-7%
Tensile tear resistance	ASTM D-624	4-7 kg/cm	4-7 kg/cm

FIGURE 8.16 Data sheet of Agilus30.

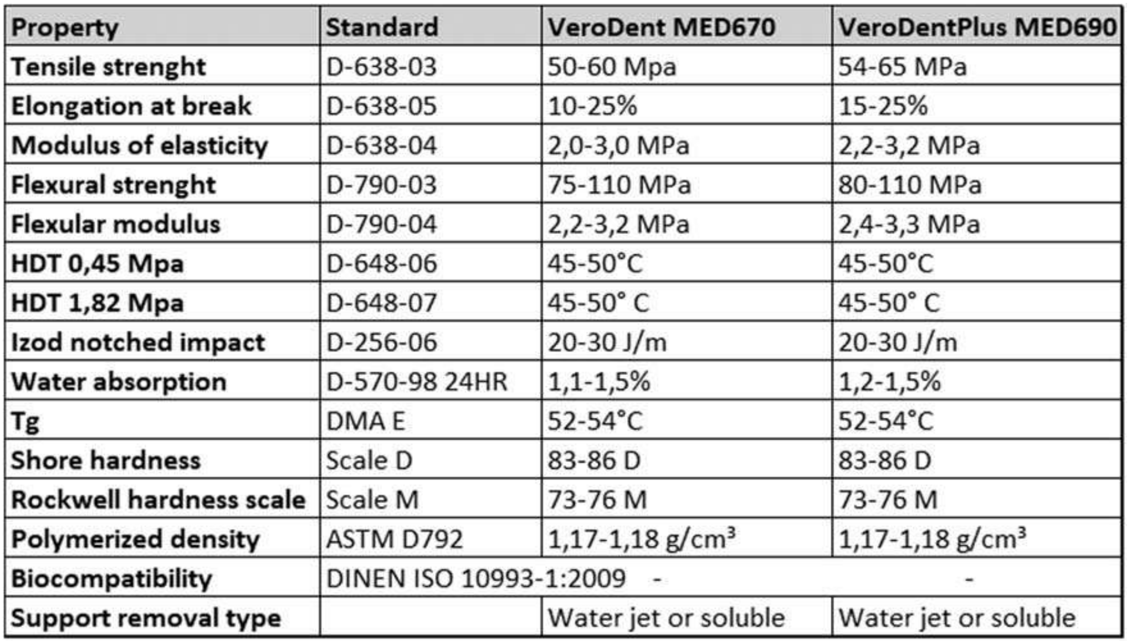


Property	Standard	Value
Tensile strenght	D-638-03	50-65 Mpa
Elongation at break	D-638-05	10-25%
Modulus of elasticity	D-638-04	2-3 MPa
Flexural strenght	D-790-03	75-110 MPa
Flexular modulus	D-790-04	2,2-3,2 MPa
HDT 0,45 Mpa	D-648-06	45-50°C
HDT 1,82 Mpa	D-648-07	45-50° C
Izod notched impact	D-256-06	20-30 J/m
Water absorption	D-570-98 24HR	1,1-1,5%
Tg	DMA E	52-54°C
Shore hardness	Scale D	83-86 D
Rockwell hardness scale	Scale M	73-76 D
Polymerized density	ASTM D792	1,17-1,18 g/cm³
Biocompatibility	prEN ISO 10993-1	Skin contact- permanent (>30 days) Mucous membrane -short term (up to 24 hrs)
Sterilization methods		Gamma sterilization using a dose of 25-50 kGy Steam sterilization for 4 minutes at 132°C with fractioned pre-vacuum
Support removal type		Water jet or soluble

FIGURE 8.17 MED610 data sheet.

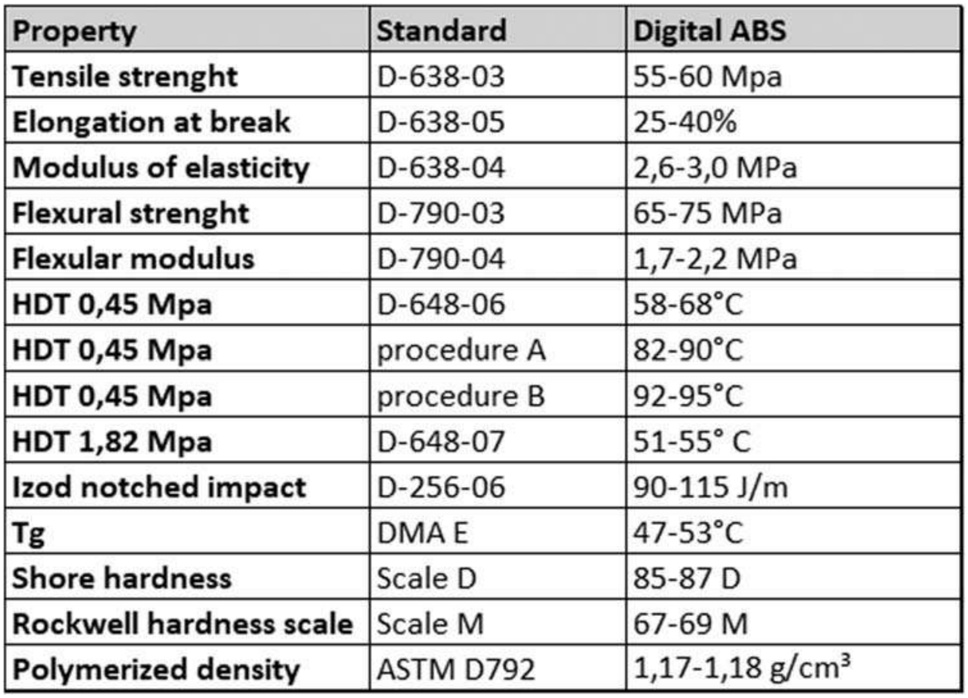
Biocompatible materials, like MED610 for dental and medical purpose, are often transparent. They can be flexible or rigid (Fig. 8.17). They are safe for skin (up to 24 h contact); they can be used for implant or orthopedic. Their minimum layer thickness is 16 microns and their heat deflection temperature (HDT) is 45–50°C, regardless of load [8].

There are also typical dental materials, like VeroDent series. They are created for orthodontic labs and clear aligner manufacturers. Their main advantages are: strength, durability in tone, high-quality detail (Fig. 8.18). VeroDent Plus



Property	Standard	VeroDent MED670	VeroDentPlus MED690
Tensile strenght	D-638-03	50-60 Mpa	54-65 MPa
Elongation at break	D-638-05	10-25%	15-25%
Modulus of elasticity	D-638-04	2,0-3,0 MPa	2,2-3,2 MPa
Flexural strenght	D-790-03	75-110 MPa	80-110 MPa
Flexular modulus	D-790-04	2,2-3,2 MPa	2,4-3,3 MPa
HDT 0,45 Mpa	D-648-06	45-50°C	45-50°C
HDT 1,82 Mpa	D-648-07	45-50° C	45-50° C
Izod notched impact	D-256-06	20-30 J/m	20-30 J/m
Water absorption	D-570-98 24HR	1,1-1,5%	1,2-1,5%
Tg	DMA E	52-54°C	52-54°C
Shore hardness	Scale D	83-86 D	83-86 D
Rockwell hardness scale	Scale M	73-76 M	73-76 M
Polymerized density	ASTM D792	1,17-1,18 g/cm³	1,17-1,18 g/cm³
Biocompatibility	DINEN ISO 10993-1:2009	-	-
Support removal type		Water jet or soluble	Water jet or soluble

FIGURE 8.18 VeroDent data sheet.



Property	Standard	Digital ABS
Tensile strenght	D-638-03	55-60 Mpa
Elongation at break	D-638-05	25-40%
Modulus of elasticity	D-638-04	2,6-3,0 MPa
Flexural strenght	D-790-03	65-75 MPa
Flexular modulus	D-790-04	1,7-2,2 MPa
HDT 0,45 Mpa	D-648-06	58-68°C
HDT 0,45 Mpa	procedure A	82-90°C
HDT 0,45 Mpa	procedure B	92-95°C
HDT 1,82 Mpa	D-648-07	51-55° C
Izod notched impact	D-256-06	90-115 J/m
Tg	DMA E	47-53°C
Shore hardness	Scale D	85-87 D
Rockwell hardness scale	Scale M	67-69 M
Polymerized density	ASTM D792	1,17-1,18 g/cm³

FIGURE 8.19 Digital ABS data sheet.

is more durable than VeroDent — it has higher tensile strength and elongation at break. What is more, its modulus of elasticity, flexural strength, and modulus have also higher values [8].

Digital ABS plus is created for standard ABS plastic simulation. It is resistant on high temperature; it can be used in tools and electrical parts production (Fig. 8.19). Digital ABS has different HDT for the same loads because of thermal posttreatment procedures (A or B). Namely, it increases from 58°C (without posttreatment) up to 95°C [8].

8.4 Advantages and disadvantages

8.4.1 *Advantages and disadvantages of MJP*

MJP is profitable because it uses cheap materials. Its advantage is also exactness – MJP creates prototypes in high definition (the resolution is 750 × 750 × 1600 dpi). Machines are fast – they are able to build elements very quickly. They are easy to use and they don't need any complicated programs.

However, this technology has also disadvantages. MJP machines can build only small elements and they are limited to use thermopolymers [2].

On the one hand, time of job realization of MJP technology is faster than in case of molded wax patterns (Fig. 8.20). On the other hand, when the number of patterns is big (depending on type of printer), there is a time breakeven. It means that faster method becomes this analogue one (molded wax) [5].

Total pattern cost is also connected with number of patterns (Fig. 8.21). Cost of molded wax patterns is very big, bigger than in case of 3D printing parts, when their number is small. However, more patterns are made, lower cost of analogue parts is generated [5].

8.4.2 *Advantages and disadvantages of PJ*

PolyJet printing has very good resolution and accuracy. Layers are ultrathin (i.e., 16 μm) and pattern does not have to be postcured; it is able to be handled immediately. In this technique different materials can be used and surface of prototypes is smooth. However, PolyJet printing is more expensive than other 3D methods (Fig. 8.22) [11]. What is more, edges of model are not as sharp as they should be, they can be slightly rounded [12].

8.5 Concluding remarks and future insight

The comparison of PJM and MJM is presented in the table (Fig. 8.23). A layer thickness is the same for two methods. Both use printhead to deposit material. However, there is a material support difference. In case of PolyJet it has more complicated composition (propylene, acrylic monomer, polyethylene, glycerin); for Multi Jet is very simple because it's only paraffin wax. What is more, in PJM is more difficult to remove unnecessary parts. The final element has to be immersed in a chemical compound. In MJM method removal process is easier and chemicals application is redundant.

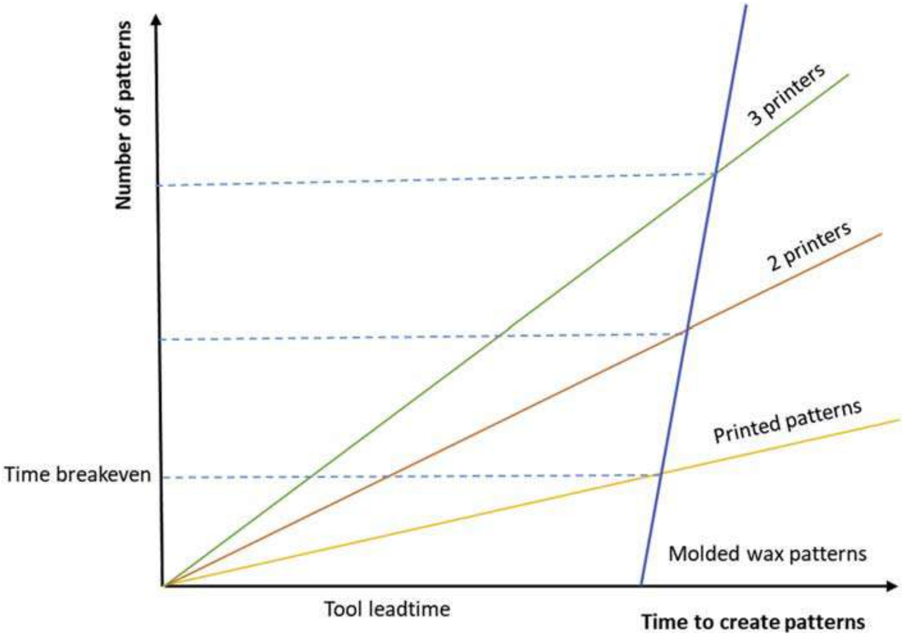


FIGURE 8.20 Molded wax pattern versus 3D printed patterns – time breakeven.

FIGURE 8.21 Molded wax pattern versus 3D printed patterns — cost breakeven.

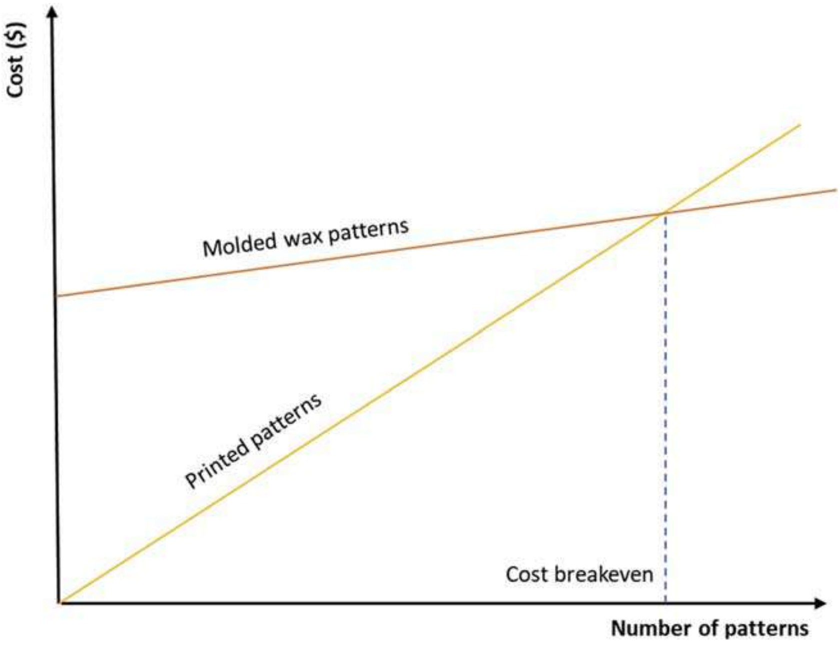
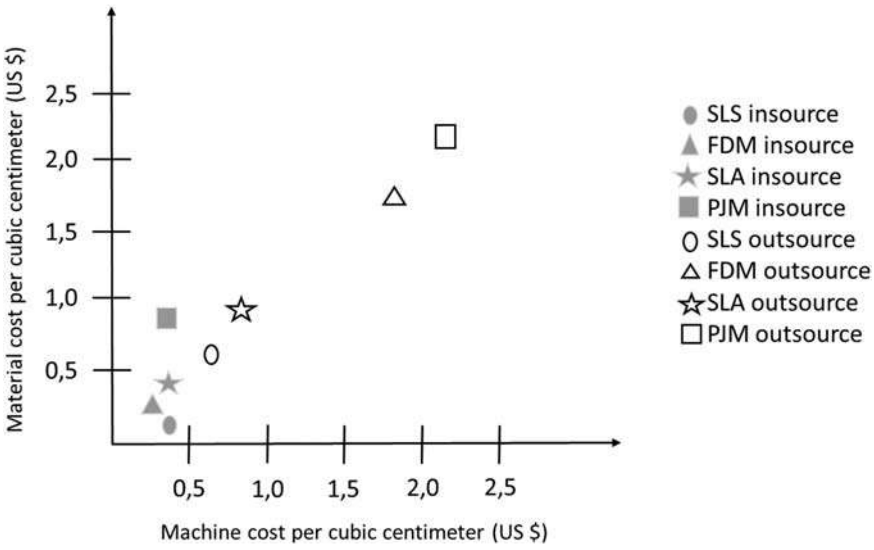
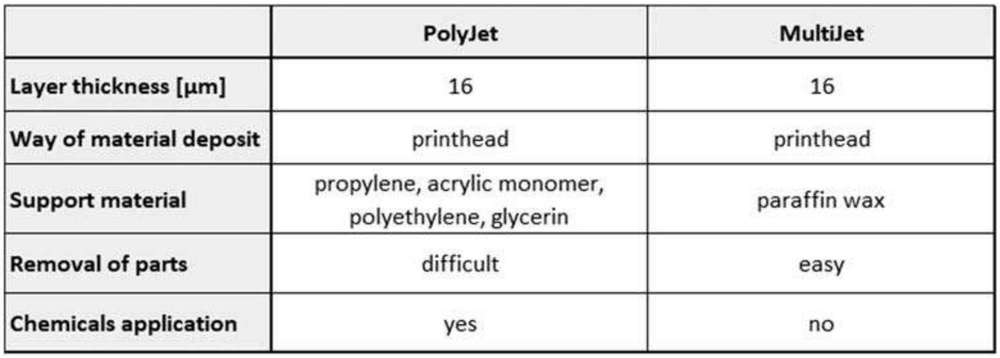


FIGURE 8.22 Cost of material and machine per cubic centimeter — comparison between different 3D methods (*SLA*, stereolithographic; *SLS*, selective laser sintering; *FDM*, fused deposition modeling; *PJM*, PolyJet modeling).





	PolyJet	MultiJet
Layer thickness [µm]	16	16
Way of material deposit	printhead	printhead
Support material	propylene, acrylic monomer, polyethylene, glycerin	paraffin wax
Removal of parts	difficult	easy
Chemicals application	yes	no

FIGURE 8.23 PJM and MJM comparison.

To sum up, MJM and PJM are very similar, although they are produced by two different companies. Their biggest advantage is accuracy and high resolution. The production cycle in 3D printing is very short. The main disadvantage is cost of materials – both methods are the most expensive in 3D technologies. Both can be used in health, construction, and manufacturing industry. They are very modern and still developed; this is the reason why their cost can be lower in the near future.

References

[1] C. Coward, 3D Printing, Penguin, 2015.

[2] C.K. Chua, K.F. Leong, 3D Printing and Additive Manufacturing: Principles and Applications, World Scientific, 2014, pp. 60–68.

[3] M. Schönberger, M. Hoffstetter. Emerging Trends in Medical Plastic Engineering and Manufacturing, Elsevier, 2016, p. 122.

[4] A.C. Taylor, System and Process Development for a Coaxial Extrusion. Nozzle for Fused Deposition Modelling, Master of thesis, University of Wollongong, 2015, p. 8.

[5] 3D Systems, Inc., Product information, www.3dsystems.com (Accessed 14 March 2020).

[6] 3D Printing Industry, Colour and multi-materials 3d Systems pre-euromold announcements, Rachel Park, www.3dprintingindustry.com (Accessed 14 March 2020).

[7] D.M. Kalaskar, 3D Printing in Medicine, Elsevier, 2017.

[8] Stratasys, Product information, www.stratasys.com (Accessed 28 March 2020).

[9] K.-Y. Lee, J.-W. Cho, Accuracy of three-dimensional printing for manufacturing replica teeth, Korean J. Orthod. 45 (2015) 217–225.

[10] C. Seunghee, Advances in Research and Clinical Approaches to Functional Restoration, Springer, 2017, p. 176.

[11] M. Kutz, Applied Plastics Engineering Handbook: Processing, Materials, and Applications, Elsevier, 2016, p. 631.

[12] M.E. Hoque, Advanced Applications of Rapid Prototyping Technology in Modern Engineering, Intech, 2011, p. 188.

CHAPTER

9

Powder bed fusion

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9.1 Method introduction

Selective laser sintering (SLS) or selective laser melting (SLM) is part of so-called powder bed fusion group of methods. The group includes at least four methods: electron beam melting (EBM), Multi Jet Fusion (MJF), SLS, and SLM. EBM is a method dedicated to metallic powders due to their electronic conductivity necessary to carry on the process. MJF is related to narrow group of polyamides (PA 11 and PA 12), polypropylene (PP), and thermoplastic polyurethane (TPU), and the physical properties of the 3D printed parts are different from typical due to application of additional agents. SLS and SLM methods were here described in detail due to their polymer material versatility and 3D printed parts engineering functionality due to their properties comparable to typical polymer materials.

Sintering is a surface tension–driven process that occurs in temperatures below the melting point. The most significant phenomena in this process are diffusion (atomic migration) and fusion of the powder particles that create solid mass. The powder particles cannot be fully fused during the sintering process and thus the volume of the sintered parts can have some pores. It can have some negative impact on mechanical properties of the 3D printed parts. SLM process is carried in temperatures ensuring polymer particles melting and complete fusion but is difficult to control due to liquid phase specific limitations (i.e., balling effect, polymer excessive degradation, etc.) [1]. Nevertheless, if the process is conducted in a controlled way the physical properties of the SLM 3D printed parts are comparable with SLS printed parts as the porosity is still observed [2].

The 3D part is built based on a CAD (computer-aided design) file. Usually, the designed part has to be exported to format (STL, Standard Triangle Language) that describes only the surface of a three-dimensional model. Then the object has to be sliced into a sequence of layers and laser paths have to be defined before the process starts (see Fig. 9.1) [3,4]. Unlike in SLS and SLM of metallic powders the supporting structures are not required in case of polymer powder processing as residual stress is negligible [5]. The laser beam path is then calculated for precise filling of each cross section (see Fig. 9.2).

As it was depicted beneath in Fig. 9.2, suitable laser energy deposition in the polymer powder layer requires in-depth understanding of the phenomena occurring in this stage and proper laser beam manipulation. Constant laser beam scanning speed over the powder bed is crucial for equal energy deposition that has impact on material behavior, process reliability, repeatability, and printed 3D parts size and shape accuracy. Complete program for the sequences of layers and laser beam paths is generated and transferred to the 3D printer. The schemes of various machine systems are presented in Fig. 9.3A and B.

The process is realized as presented in Fig. 9.4.

Once the 3D part is printed and removed from the working chamber, it has to be carefully cleaned with brush, compressed air, and finally shot peened for smoothing the surface with silica glass micropowder. After cleaning and shot peening the part is ready for use or further postprocessing like painting.

The most important factors having impact on the 3D printed part quality and accuracy are:

- design according to the guidelines,
- 3D CAD file quality (some CAD 3D systems enable definition of a triangle size of STL file),
- the chosen (available) layer thickness,
- shrinkage and warping [10–12].

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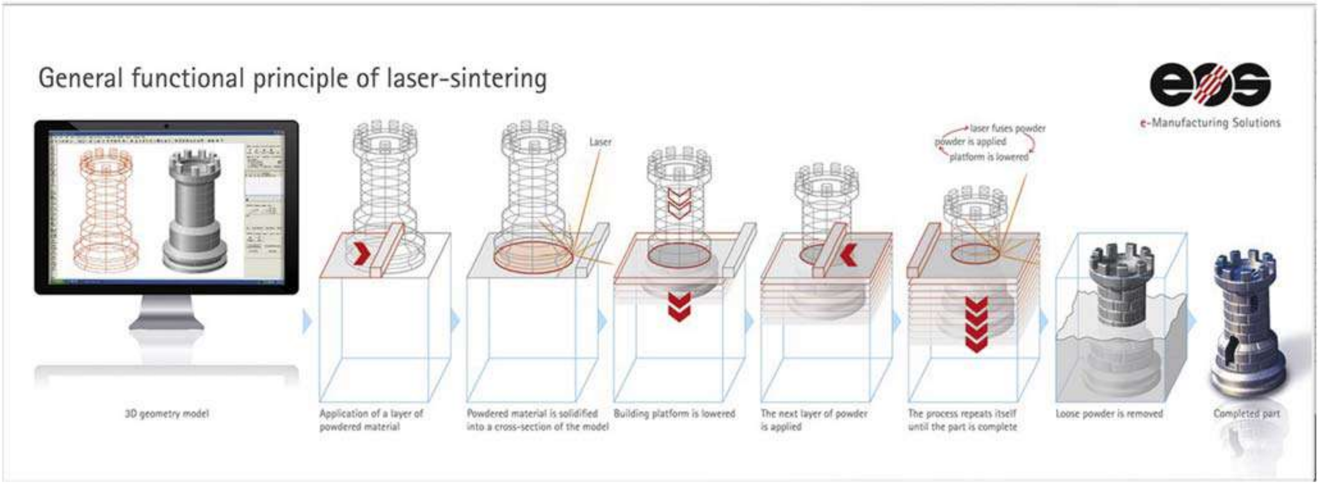


FIGURE 9.1 Scheme of CAD file slicing into a sequence of predefined layers for 3D printing [6].

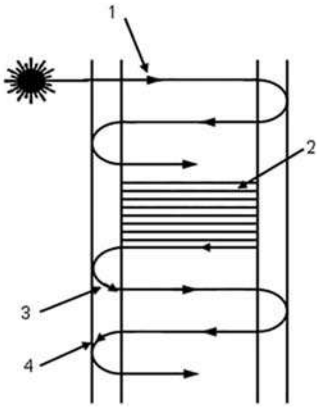


FIGURE 9.2 Schematic of a CAD file cross section filling. (1) Direction of laser beam, (2) layer building area – filling (laser beam is delivered to the powder bed), (3) laser beam deceleration phase (laser beam is not delivered to the powder bed), (4) laser beam acceleration phase (laser beam is not delivered to the powder bed).

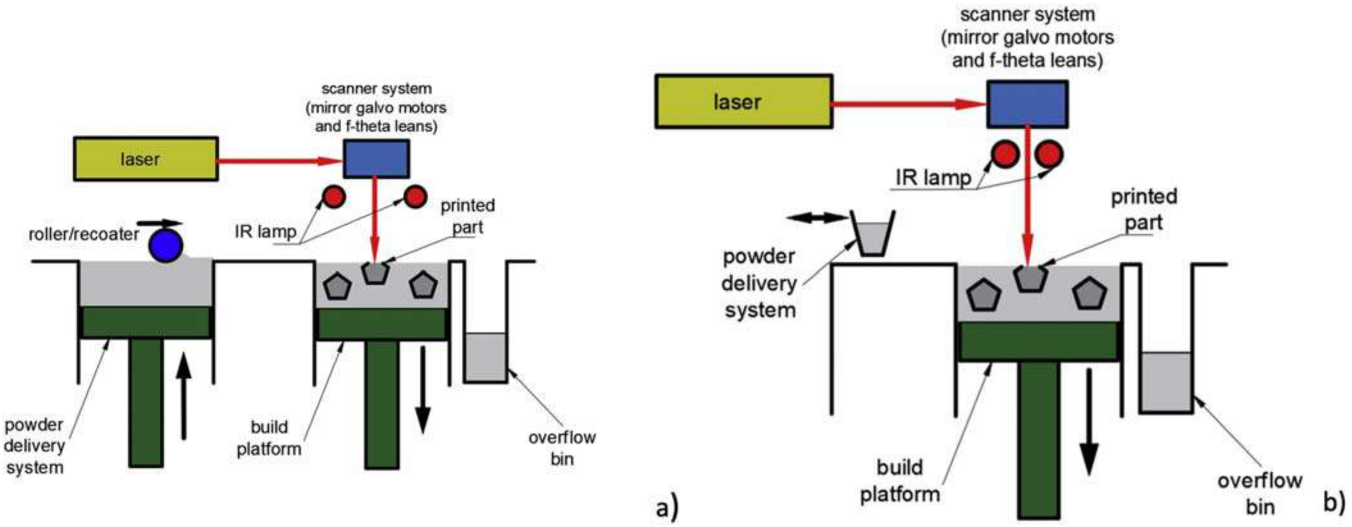
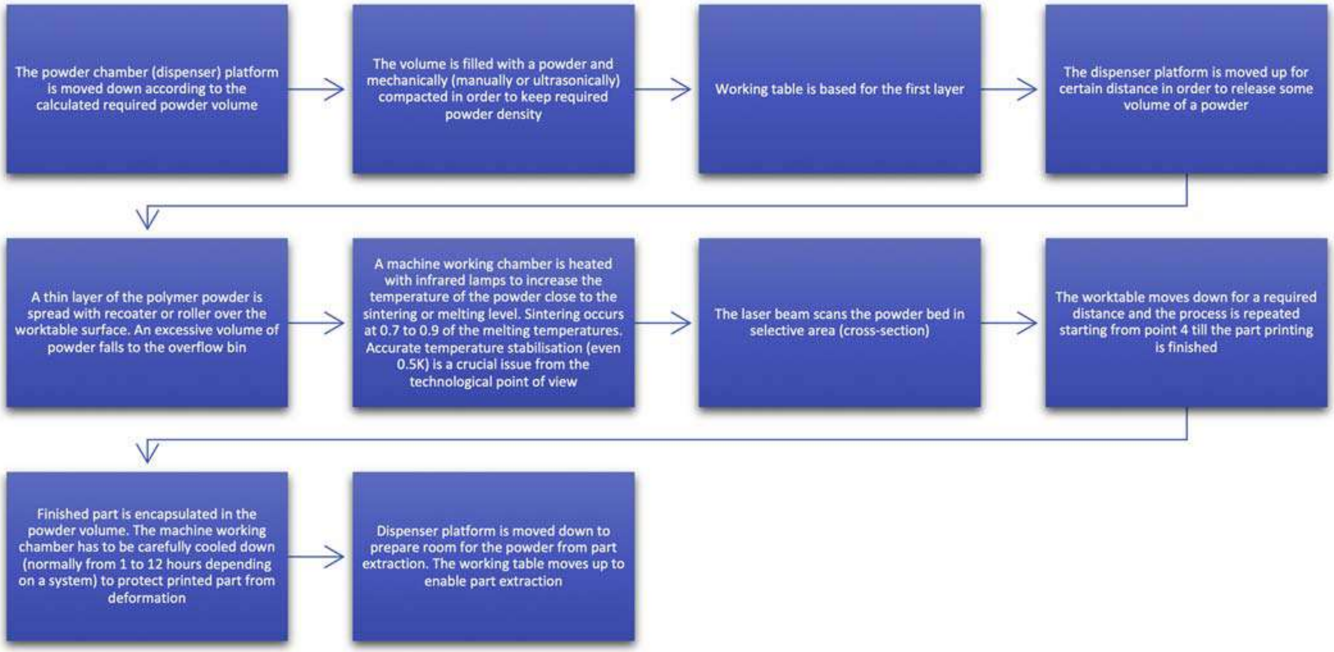


FIGURE 9.3 Schemes of the most common SLS/SLM systems: (A) side feeding, (B) top feeding.



The powder chamber (dispenser) platform is moved down according to the calculated required powder volume

The volume is filled with a powder and mechanically (manually or ultrasonically) compacted in order to keep required powder density

Working table is based for the first layer

The dispenser platform is moved up for certain distance in order to release some volume of a powder

A thin layer of the polymer powder is spread with recoater or roller over the worktable surface. An excessive volume of powder falls to the overflow bin

A machine working chamber is heated with infrared lamps to increase the temperature of the powder close to the sintering or melting level. Sintering occurs at 0.7 to 0.9 of the melting temperatures. Accurate temperature stabilisation (even 0.5K) is a crucial issue from the technological point of view

The laser beam scans the powder bed in selective area (cross-section)

The worktable moves down for a required distance and the process is repeated starting from point 4 till the part printing is finished

Finished part is encapsulated in the powder volume. The machine working chamber has to be carefully cooled down (normally from 1 to 12 hours depending on a system) to protect printed part from deformation

Dispenser platform is moved down to prepare room for the powder from part extraction. The working table moves up to enable part extraction

FIGURE 9.4 Typical algorithm for SLS/SLM process. (Source: *Own elaboration on the basis* [7–9]).

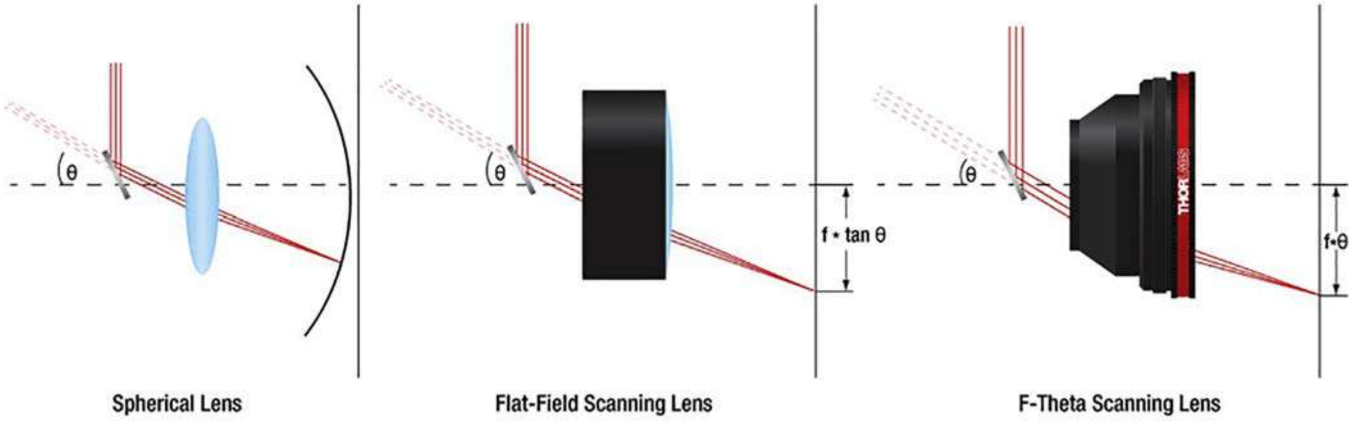


FIGURE 9.5 Scheme of f-theta lens compared to the common focusing lens [13].

Most of the SLS and SLM systems use CO_2 laser (the wavelength $\lambda = 10{,}640$ nm, power $P =$ up to 70 W for polymers) as an energy source and galvo motors equipped with mirrors for laser beam scanning over the powder bed. The applied in such a systems laser beam sources have very good beam quality (Gaussian energy distribution in a cross section that has significant impact on 3D printed part quality). This solution requires application of so-called f-theta lens that enables correction of the laser beam profile deformation and control of a focal distance (or depth of focus). The scheme of the f-theta lens compared to common lens is presented in Fig. 9.5.

Application of the focusing lens is necessary to obtain laser energy density necessary for powder bed sintering or melting. The focused laser beam is also very precise tool for cross section contour printing that has important impact on the 3D printed part precision, accuracy, and detail definition. The scheme of the cross section filling with the use of f-theta lens was presented in Fig. 9.6.

It is worth to underline that laser beam scanning speed can be varied depending on the scanned area. Typically scanning speed is about 7 m/s and the focused laser beam spot is about 300 μm. Average working chamber capacity of such a system starts from 300 mm × 300 mm × 300 mm to 750 mm × 550 mm × 550 mm. The working chamber capacity has a serious impact on a complete part's printing time. The larger volume the longer preheating and cooling down time. Also material type has impact on cooling time ratio. In example for Sinterit machine for the same part total time preheating and cooling down time for FlexaBlack is 2 h shorter than for PA 12 (ca. three times faster). This time difference has serious impact on cost and delivery time for small parts and low number series.

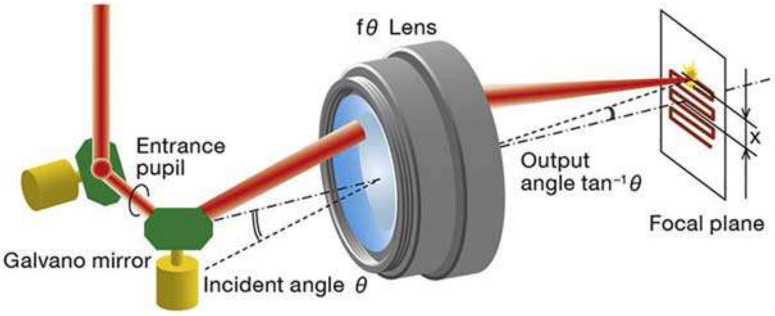


FIGURE 9.6 Scheme of the single layer cross section filling with the use of f-theta lens [14].

9.2 SLS systems

SLS was patented and has been developed for almost 40 years. During this time the method was evaluated and developed in order to achieve better printed part accuracy, precision, and properties. The patent protection has finished recently, and one can observe many variations of the system solution. The most common are those presented in Fig. 9.3A and B but many other interesting could be observed too. The example of different SLS system solution is presented in Fig. 9.7.

The below-presented system is developed by many worldwide manufacturers. The most important difference is a kinematic solution. The laser beam is delivered through the standard focusing lens directly and perpendicularly to the powder surface. This solution is much cheaper as no expensive galvo mirror scanner and f-theta lens is applied but the scanning speed is much lower compared to the standard systems. The laser source is moved together with focusing lens over the powder bed with use of gantry system. The scheme of such a system is presented in Fig. 9.8.

In this case the laser beam scanning speed is low (compared to standard systems) which means that less laser power is required to melt or sinter the polymer powder layer. Typically, the systems are equipped with cheaper semiconductor laser diodes ($\lambda = 808-1080$ nm, $P = 1-10$ W). The semiconductor laser beam has also quasi-Gaussian energy distribution in a cross section (is more rectangular than round) that can also have impact on printed

FIGURE 9.7 SLS system without galvo motors and f-theta lens: (A) Sinterit, (B) Sintratec [15,16].

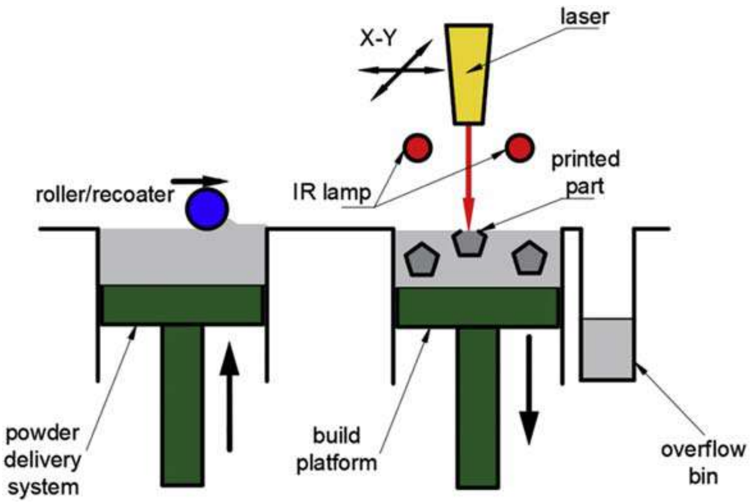


FIGURE 9.8 Scheme of the SLS/SLM gantry-based system.

FIGURE 9.9 Selective laser sintered parts made of PA 12. (Source: *own elaboration).*

part quality. The working chamber of such a system also has to be preheated (for a period of about 2 h) to the temperature close to the sintering/melting point of the powder material and then maintained all over the printing process with high accuracy reaching 0.5 K. When the printing is finished the temperature is slowly decreased (for about 1 h) in order to avoid excessive deformations of the printed part. Some examples of the 3D printed parts are depicted in Fig. 9.9.

9.3 Advantages and disadvantages of powder bed fusion

One of the most significant advantages of the SLS/SLM of thermoplastic powders is that there is no need for supporting structures that could be observed in other additive manufacturing methods. This is related to negligible residual stress remaining in the 3D in printed parts after the process. (The residual stress has strong impact on 3D printed parts shape and size accuracy in case of SLS and SLM of metallic parts.) Thus the whole volume of the working chamber can be filled with printed parts. The solution was presented in Fig. 9.10.

Another positive aspect of PBF is ability to use versatility of powder materials and sustainable material management and recyclability. In PBF group of methods almost no material is lost. As no supporting structures are required the material is consumed for part building only. Some powder material is lost during the process due to handling and cleaning, but the amount is negligible. The life cycle of the 3D printed parts in this case is environmentally friendly. The manufacturing process is energy and material efficient, and the applied polymers can be easily recycled with no harm and waste.

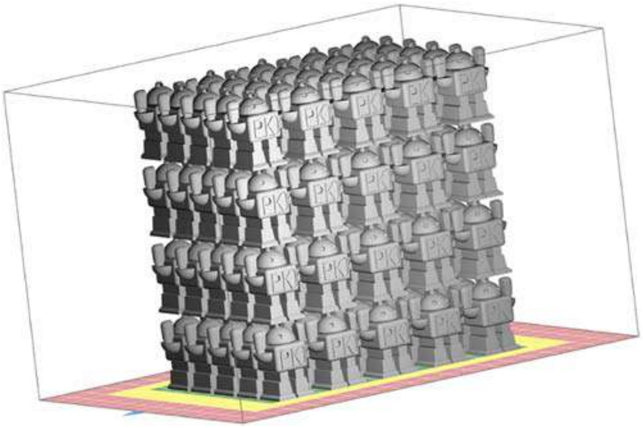


FIGURE 9.10 Working chamber volume fully filled with printed models. (Source: *Own elaboration on the basis [17]).*

It is worth to underline that polymer powder bed fusion methods like SLM and SLS despite numerous advantages have some drawbacks:

- postprocessing (cleaning, shot peening),
- limited accessibility of engineering materials,
- manufactured parts have to be designed according to the specific rules that enable printability, accuracy, and possibility of part assembling,
- polymer powders are highly prone for electrostatic charge accumulation and there is a risk of electrical discharge that can cause combustion or explosion − therefore special working chamber cleaning equipment is required.

9.4 Materials for powder bed fusion

SLS and SLM methods give quite a wide range polymer material that can be applied for 3D part printing. Table 9.1 presents the most common groups of materials offered by EOS, Germany.

It is worth to emphasize that polymer materials used in SLS and SLM processes lose their original properties due to heat impact, and the powder volume requires refilling with some volume of fresh material. The amount of the fresh powder added to the original volume depends on polymer type, process parameters, and volume of the 3D printed parts. Refreshing provides required printed parts shape and size accuracy, mechanical properties, as well as the successful 3D printing process.

Very important drawback of the polymer powders used in SLS and SLM processes is their hygroscopicity. Good practice is to store the unused powders in dry and sealed containers. The dry powder provides required in the process flowability and bulk density that have essential impact on the 3D printing process reliability and repeatability.

9.5 Concluding remarks and future insight

SLS and SLM methods have been developed for recent couple of decades. In this time many kinematic solutions have been proposed. Currently several various systems are available on the market. Some of them, like these offered by EOS GmbH, are addressed for professional and industrial applications; others like from Sinterit or Sintratec are tailored for small and medium enterprises, research and development laboratories of companies and universities. There is a wide variety of systems:

- starting from small building volume (90 m × 130 m × 130 m), gantry moved 5 W power laser diode ($\lambda = 808$ nm) of low building rate, layer thickness 0.075 mm−0.175 mm,
- going through medium size (340 m × 340 m × 600 m), single laser source (CO_2, $P = 70$ W) and relatively low building rate (48 mm/h), layer thickness 0.06 mm, and
- finishing on large capacity (700 m × 380 m × 380 m) dual (CO_2 $P = 2 \times 70$ W) laser scanning systems of high building rate reaching 2.7 L/h (layer thickness 120 μm).

TABLE 9.1 The most common polymers used for SLS 3D part printing [6].

<table>
<tr><th colspan="4">Material</th></tr>
<tr><th colspan="4">Alumide - PA12-MED(Al)</th></tr>
<tr><th>Description</th><th>Application</th><th>Finishing</th><th>Properties</th></tr>
<tr>
<td>Metallic gray, aluminum-filled polyamide 12 powder, which is characterized by its high stiffness, metallic appearance and good postprocessing possibilities.
Laser-sintered parts made from Alumide possess excellent material properties:
- excellent dimensional accuracy,
- well-balanced ratio of density and stiffness, and
- increased thermal conductivity good machinability.</td>
<td>- Manufacture of stiff parts of metallic appearance for applications in automotive manufacture (e.g., wind tunnel tests or parts that are not safety-relevant),
- for tool inserts for injecting and molding small production runs,
- for illustrative models (metallic appearance), and
- for education and jig manufacture et al.</td>
<td>- Surfaces of Alumide parts can be refined very easily by grinding, polishing, or coating. The machining of Alumide laser-sintered parts is simplified through the cut breaking effect of the aluminum filling.</td>
<td>
<table>
<tr><th>Mechanical</th><th>Value</th><th>Unit</th><th>Test Standard</th></tr>
<tr><td>Tensile modulus</td><td>3800</td><td>MPa</td><td>ISO 527</td></tr>
<tr><td>Tensile strength</td><td>48</td><td>MPa</td><td>ISO 527</td></tr>
<tr><td>Strain at break</td><td>4</td><td>%</td><td>ISO 527</td></tr>
<tr><td>Charpy impact strength (+23°C)</td><td>29</td><td>kJ/m²</td><td>ISO 179/1eU</td></tr>
<tr><td>Charpy notched impact strength (+23°C)</td><td>4.6</td><td>kJ/m²</td><td>ISO 179/1eA</td></tr>
<tr><td>Flexural modulus (23°C)</td><td>3600</td><td>MPa</td><td>ISO 178</td></tr>
<tr><td>Flexural Strength</td><td>72</td><td>MPa</td><td>ISO 178</td></tr>
<tr><td>Shore D hardness</td><td>76</td><td>–</td><td>ISO 7619-1</td></tr>
<tr><th>Thermal</th><th>Value</th><th>Unit</th><th>Test Standard</th></tr>
<tr><td>Melting temperature (20°C/min)</td><td>176</td><td>°C</td><td>ISO 11357-1/-3</td></tr>
<tr><td>Temp. of deflection under load</td><td></td><td></td><td>ISO 75-1/-2</td></tr>
<tr><td>1.80 MPa</td><td>144</td><td>°C</td><td></td></tr>
<tr><td>0.45 MPa</td><td>175</td><td>°C</td><td></td></tr>
<tr><td>Vicat softening temperature (50°C/h 50N)</td><td>169</td><td>°C</td><td>ISO 306</td></tr>
<tr><th>Electrical</th><th>Value</th><th>Unit</th><th>Test Standard</th></tr>
<tr><td>Relative permittivity</td><td></td><td></td><td>IEC 62631-2-1</td></tr>
<tr><td>100Hz</td><td>13</td><td>–</td><td></td></tr>
<tr><td>1MHz</td><td>10</td><td>–</td><td></td></tr>
<tr><td>Dissipation factor (1MHz)</td><td>180</td><td>E-4</td><td>IEC 62631-2-1</td></tr>
<tr><td>Volume resistivity</td><td>3,00E+12</td><td>Ohm·m</td><td>IEC 62631-3-1</td></tr>
<tr><td>Surface resistivity</td><td>5,00E+14</td><td>Ohm</td><td>IEC 62631-3-2</td></tr>
<tr><td>Electric strength</td><td>0.1</td><td>kV/mm</td><td>IEC 60243-1</td></tr>
</table>
The properties of parts manufactured using selective laser sintering are, due to their layer-by-layer production, to some extent direction dependent. This must be considered when designing the part and defining the build orientation.
</td>
</tr>
<tr><th colspan="4">CarbonMide - PA12-CF</th></tr>
<tr>
<td>Anthracite black, carbon-fiber-filled polyamide 12 material stands out for excellent stiffness and a maximized weight–strength ratio.
Laser-sintered parts made from CarbonMide possess excellent material properties:

- extreme stiffness,
- excellent strength and hardness,
- light weight, and
- electric conductivity.</td>
<td>Mechanically stressed parts which are optimized considering the self-weight of the part. Components in motor sports application.</td>
<td>Surface finished CarbonMide parts are suited for, e.g., usage as aerodynamic.</td>
<td>Due to the process related orientation of the fibers the mechanical properties vary in the three axes directions.</td>
</tr>
<tr><th colspan="4">EOS PEEK HP3 - PEEK</th></tr>
<tr>
<td>High-performance polymer belonging to the group of Polyaryletherketone (PAEK), semi-crystalline, thermoplastic material. Outstanding combinations of properties are:
- excellent high-temperature, performance,
- high wear resistance,
- outstanding chemical resistance,
- best fire, smoke, and toxicity performance,
- good hydrolysis resistance,
- potential biocompatibility, and
- sterilizability.</td>
<td>Medicine, aerospace industry, or motorsports.
In medical applications the outstanding properties make this material an ideal replacement for stainless steel and titanium.
In aerospace and in motorsports, light weight and fire resistance are of largest importance; EOS PEEK HP3 has developed to an adequate metal replacement.</td>
<td>–</td>
<td>
<table>
<tr><th>Mechanical</th><th>Value</th><th>Unit</th><th>Test Standard</th></tr>
<tr><td>Tensile modulus</td><td>4250</td><td>MPa</td><td>ISO 527</td></tr>
<tr><td>Tensile strength</td><td>90</td><td>MPa</td><td>ISO 527</td></tr>
<tr><td>Strain at break</td><td>2.8</td><td>%</td><td>ISO 527</td></tr>
<tr><th>Thermal</th><th></th><th></th><th></th></tr>
<tr><td>Melting temperature (20°C/min)</td><td>372</td><td>°C</td><td>ISO 11357-1/-3</td></tr>
<tr><td>Temp. of deflection under load (1.80 MPa)</td><td>165</td><td>°C</td><td>ISO 75-1/-2</td></tr>
<tr><th>Other</th><th></th><th></th><th></th></tr>
<tr><td>Density (laser sintered)</td><td>1310</td><td>kg/m³</td><td>EOS Method</td></tr>
</table>
</td>
</tr>
<tr><th colspan="4">PA 11</th></tr>
<tr>
<td>Made from renewable raw materials (castor oil).
Properties:
- high elongation at break,
- elasticity,
- high impact resistance,
- excellent resistance to chemicals like:
- hydrocarbons, aldehydes,
- ketones, mineral bases, and salts,
- alcohols, and
- fuels, detergents, oils, and fats.</td>
<td>Mechanically loaded functional prototypes and series parts with long-term moving elements (e.g., hinges):
- In the automotive industry, it is mainly used for interior components for crash relevant parts (PA 1101 components do not splinter)
- Especially suited for small to medium sized parts, thin walls, and lattice structures.</td>
<td>–</td>
<td>
<table>
<tr><th>Mechanical</th><th>Value</th><th>Unit</th><th>Test Standard</th></tr>
<tr><td>Tensile modulus</td><td>1600</td><td>MPa</td><td>ISO 527</td></tr>
<tr><td>Tensile strength</td><td>48</td><td>MPa</td><td>ISO 527</td></tr>
<tr><td>Strain at break</td><td>45</td><td>%</td><td>ISO 527</td></tr>
<tr><td>Charpy notched impact strength (+23°C)</td><td>7.8</td><td>kJ/m²</td><td>ISO 179/1eA</td></tr>
<tr><td>Shore D hardness</td><td>75</td><td>–</td><td>ISO 7619-1</td></tr>
<tr><th>Other</th><th></th><th></th><th></th></tr>
<tr><td>Density (laser sintered)</td><td>990</td><td>kg/m³</td><td>EOS Method</td></tr>
</table>
</td>
</tr>
</table>

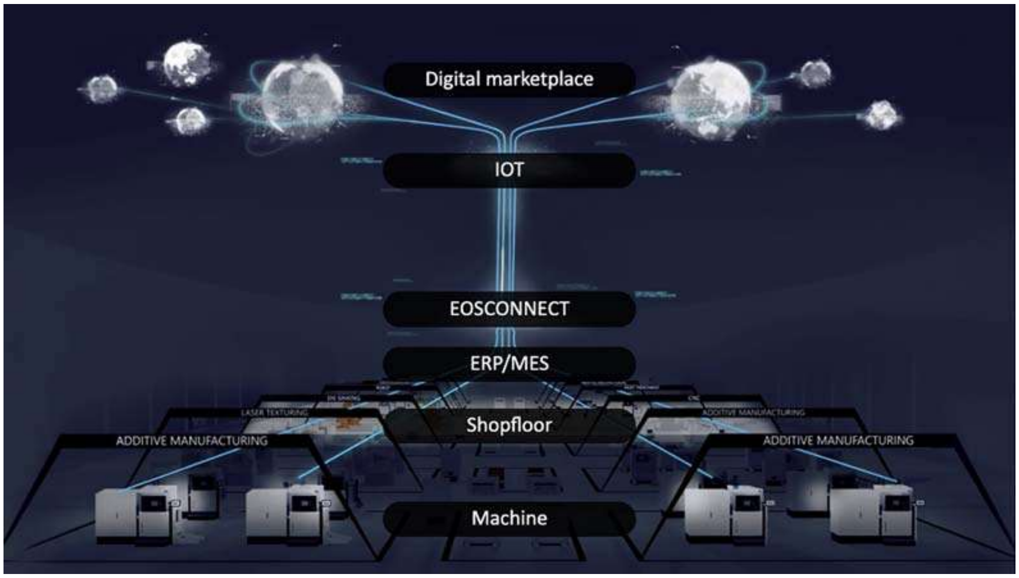


FIGURE 9.11 Scheme of fully integrated additive manufacturing into production line that can be seamlessly connected to Manufacturing Execution System (MES) or Enterprise Resource Planning (ERP) solutions on site, but they can also serve the digital marketplaces and IoT platforms of the future [6].

The goal of the current development in this field is possibility of implementation of the additive manufacturing system into the production line in accordance to INDUSTRY 4.0 [18,19]. Such a solution is presented in Fig. 9.11.

The future of additive manufacturing of polymer material could be a system designed for maximum productivity with a constant focus on high-quality results that is announced to be released in 2021. The system is based on SLS/SLM method but consists of up to 1 million diode lasers with a maximum accumulated laser power of over 5 kW. LaserProFusion, because that's what this technology is called, would fit the requirements of mass production and is expected to shorten product development time. Moreover, it would enable tool-free injection molding and could replace an injection molding in many applications.

References

[1] X. Liu, Numerical Modeling and Simulation of Selective Laser Sintering in Polymer Powder Bed, Thermics [physics.class-ph], Université de Lyon, 2017–2018. English. ffNNT : 2017LYSEI012ff. fftel-01920677, https://tel.archives-ouvertes.fr/tel-01920677.
[2] S. Kumar, Selective laser sintering/melting, Comp. Mater. Process. 10 (2014) 93–134.
[3] A.D. Valino, J.R.C. Dizon, A.H. Espera, Q. Chen, J. Messman, R.C. Advincula, Advances in 3D printing of thermoplastic polymer composites and nanocomposites, Prog. Polym. Sci. 98 (2019) 1–19, 101162.
[4] S. Kumar, Additive Manufacturing Processes, Springer Nature Switzerland AG, 2020 , ISBN 978-3-030-45089-2, 2020, pp. 1-9.
[5] M. Padmakumar, Additive manufacturing of tungsten carbide hardmetal parts by selective laser melting (SLM), selective laser sintering (SLS) and binder Jet 3D printing (BJ3DP) techniques, Lasers Manuf. Mater. Process. 7 (2020) 338–371.
[6] EOS, 2020, www.eos.info (Accessed 06 June 2020).
[7] I. Gibson, Additive Manufacturing Technologies, 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing, Springer-Verlag, New York, NY, 2010, pp. 107–145.
[8] M. Schmid, Finishing of SLS-Parts for Rapid Manufacturing (RM) a Comprehensive Approach, INSPIRE, IRPD – Institute for Rapid Product Development, St. Gallen, 2009, pp. 1–10.
[9] N.N. Kumbhar, Post processing methods used to improve surface finish of products which are manufactured by additive manufacturing technologies: a review, J. Inst. Eng. India Ser. C 99 (4) (2018) 481–487.
[10] J. Allison, Powder bed fusion metrology for additive manufacturing design guidance, Addit. Manuf. 25 (2019) 239–251.
[11] B. Redwood, F. Schöffer, B. Garret, The 3D Printing Handbook: Technologies, Design and Applications, 3DHubs B.V, 2017, p. 107.
[12] B. Leutenecker-Twelsiek, Considering part orientation in design for additive manufacturing, Procedia CIRP 50 (2016) 408–413.
[13] THORLABS, 2020, www.thorlabs.com (Accessed 06 June 2020).
[14] © OptoSigma/Laser 2000, 2020, https://www.global-optosigma.com/ (Accessed 06 June 2020).
[15] SINTERIT, 2020, www.sinterit.com (Accessed 06 June 2020).
[16] SINTRATEC, 2020, www.sintratec.com (Accessed 06 June 2020).
[17] H. Sun-Min, Determination of fabricating orientation and packing in SLS process, J. Mater. Process. Technol. 112 (2001) 236–243.
[18] M.M. Mehrpouya, A. Dehghanghadikolaei, B. Fotovvati, A. Vosooghnia, S.S. Emamian, A. Gisario, The potential of additive manufacturing in the smart factory industrial 4.0: a review, Appl. Sci. 9 (18) (2019) 1–34, 3865.
[19] A. Haleem, M. Javaid, Additive manufacturing applications in industry 4.0: a review, J. Ind. Integ. Manag. Innov. Entrep. 04 (04) (2019) 1930001-1–1930001-1930023.

CHAPTER

10

Binder jetting

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10.1 Method introduction

The inkjet principle was important to the development of many additive manufacturing (AM) technologies. In particular, two concepts stand out in this universe: (1) the production of parts by direct deposition of a liquid material (usually a photopolymer, with ultraviolet curing) on a building platform, like Stratasys™ PolyJet™ technology; and (2) components obtained by blasting an agglutinating fluid over a bed of powder, forming layers as the fluid solidifies, such as the Binder Jetting (BJ) process. This last technique, due to its similarity to 2D printing, was initially called three-dimensional printing (3DP) [1,2].

Such similarity with traditional paper printing can be easily identified in several elements of the third dimension. Let us make a small set of analogies, based on the vision of the authors from the observations on the 3D printing machine (Fig. 10.1) used in the Product and Service Development Laboratory (LDPS) at Faculty of Engineering of University of Porto (FEUP).

The first common factor is that our machine uses the same ink cartridges as paper printers to deposit the binding element on the powder bed. The movements of the "3D printhead" during the construction of the profile (drawing) of the layers are the same as those performed in the printing, for example, of a picture on paper. To the naked eye, they are unique passes, unlike extrusion-based 3D printing, in which the deposition system performs a series of trajectories expelling individual filaments. Finally, the finely level and uniform layer of powder resembles a sheet of paper.

The principle of BJ technology, also known as Powder Bed Inkjet Printing, was developed around the 1990s at the Massachusetts Institute of Technology (MIT) and later marketed by companies such as ExOne™, ZCorp™ (later acquired by 3D Systems™), and Voxeljet™, using polymeric composites, metals, and ceramics as raw materials [1,3,4]. A classic model of the BJ system is shown in Fig. 10.2.

The system consists of two chambers, one for the storage and supply of fresh powder and the other for the construction of the parts. The process starts with the transfer of the powder from the feeding area to the printing area through a roller device, which is responsible not only for spreading the material, but also for the uniform leveling of the powder layer to a precise thickness. Following the actions, an inkjet head, identical to that of paper printers, blasts the binder by the thermal principle. The printhead moves along the X and Y axes depositing the liquid locally on the powder, through a set of fine jets, following the profiles originated in the slicing of the components to be produced. This fluid, therefore, reacts with the powder and thus a layer of the object is consolidated. Once this operation is completed, the building platform makes a downward movement ($-Z$ axis), equivalent to the layer thickness value, and a new batch of powder is spread over an already produced element. The deposition of binder happens again to make a new layer, which is systematic and repeated until the product is completely manufactured. It is important to mention that the powder that remains during the process is reused for other printings [1,5,6].

At the end, you get what you call a "green body". This element will be subjected to posttreatments, the most common of which are cleaning the part – vacuum up most of the unused powder on the parts, removing residual powder using brushes or a smooth jet of air – and infiltrating it to increase its mechanical strength, since the binder preserve enough the component integrity to allow its handling [3,6].

Polymers for 3D Printing
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FIGURE 10.1 FEUP's ProJet 660 PRO series machine. (Source: *courtesy of Professor Jorge Lino).*

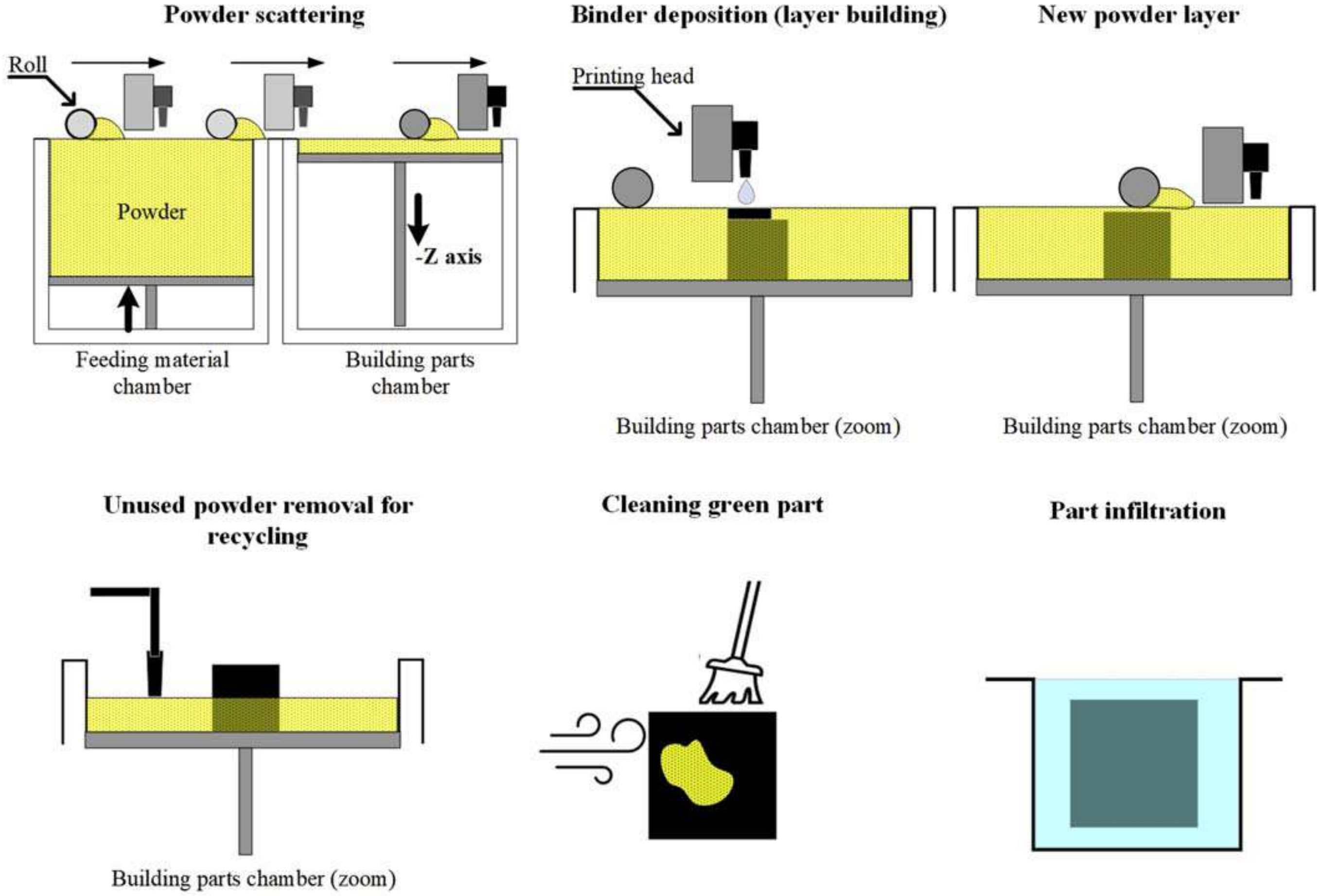

FIGURE 10.2 Binder Jetting steps. (Source: *the Authors).*

As previously mentioned, three main companies are part of the BJ scenario. 3D Systems™ markets ColorJet Printing (CJP) technology, the basis of which is the system model described so far. The main type of powder used in printers is a semihydrated calcium sulfate plaster ($CaSO_4.\ 1/2H_2O_{(s)}$), which stabilizes in its rehydrated form ($CaSO_4.\ 1/2H_2O_{(s)}$) and hardens. The applied binder is water-based and during printing loads of dyes can be

FIGURE 10.3 Chess tower in sand. (Source: *courtesy of Professor Jorge Lino*).

inserted, allowing the construction of colored pieces. The multicolored equipment has, in addition to a transparent binder, a sequence of others based on the CMYK code: cyan, magenta, yellow, and black. In the infiltration stage of the parts, materials such as waxes, cyanoacrylate (similar to superglues) (ColorBond), epoxy (StrengthMax), or an ecological option based on salt water (Salt Water Cure) can be used [1,3,7,8]. The analysis of alternative infiltrants to the options given by the printing equipment manufacturer – and its application methods – is the subject of study of different authors, which aim to open the range of material options to improve quality aspects (mechanics and coloring, among others) and reduce the costs associated with the final parts [7,9,10].

In the ExOne™ and Voxeljet™ equipment, some elements may differ from the standard as shown in Fig. 10.2, such as the presence of an auxiliary heating system, or a hopper with a blade for depositing and spreading the powder. However, they follow a methodological basis similar to the CJP process. ExOne™ operates mainly with metallic materials (titanium, steel, copper, and composites, among others), ceramics, and sands. Binders can be water-based, phenolic, solvent-based, etc. The parts produced are treated in ovens to cure the binder, sinter, and infiltrate bronze alloys, in addition to being subjected to machining, polishing, and surface treatment operations. In the case of Voxeljet™, sand and polymethylmethacrylate (PMMA) powders are generally used, the latter being capable of being finished with wax or epoxy [1,11–14]. Fig. 10.3 shows a chess piece demonstrating the ability of Voxeljet Technology™ to produce molds and cores in sand for foundry application.

In addition to the previously mentioned systems, there is also the Viridis3D RAM printer that uses the BJ principle to build sand molds for foundry. However, unlike Exone™ and Voxeljet™ systems, based on a Cartesian displacement architecture, Viridis3D™ technology uses an industrial robotic arm [15–17]. A robotic arm is also used in Mitterberger and Dermer's study [18] for BJ print structures based on biodegradable organic soil composites. In this scenario, the granular organic material is pressed in a thin layer and then a hydrogel (binder) is deposited on it following the pattern of the part. This process is repeated until the structure is complete. Finally, a postfabrication process is necessary to excavate the structure, stabilize its surface behavior, and improve its ability to respond to mechanical stresses.

10.2 Advantages and disadvantages

The main advantages and disadvantages associated with BJ technology are summarized in Table 10.1.

TABLE 10.1 Advantages and disadvantages of Binder Jetting technology [3,19–28].

Advantages	Disadvantages
Building speed: only a small portion of the total volume of parts is deposited by the printhead. In addition, the binder material is distributed simultaneously by a system consisting of multiple inkjet heads.	**Postprocessing:** indispensable. The low mechanical strength of the green bodies requires a series of operations to be carried out after the models are printed, which often implies in a much longer dedicated time than the construction of the parts (such as the sintering process in metallic elements). Postprocessing can also lead to an increase in the costs of the final process.
Economical: compared to the Selective Laser Sintering (SLS), for example, BJ is a process with lower purchase and maintenance costs for the printing device, since it uses conventional ink cartridges (paper printers) without expert modifications. The powder not used in the process is recyclable, thus reducing waste and the production cost of each part. The parts are produced without support structures, since the powder bed itself acts as a support for the development of complex geometries.	**Predictive modeling:** lack of theoretical models to predict the mechanical behavior and precision of parts.
Temperature and atmosphere: the process takes place at room temperature, thus preventing the parts from being subjected to heating and cooling cycles and, consequently, reducing the formation of thermal stress and distortions in the components. In addition, inert atmospheres or vacuum chambers are not required. These characteristics contribute to the reduction of operating costs and production of large parts.	**Dimensional aspects and surface roughness:** are usually lower than the ones of parts manufactured by other blasting materials or powder bed fusion technologies. Surfaces have a granular finish.
Scale: BJ is one of the most scalable processes and as one of the largest construction volumes among the main processes of Additive Manufacturing.	**Mechanical properties:** even after postprocessing parts still have low mechanical strength. For colored models, generally used for the visualization of concepts, this is not a big problem; however, if the objects are functional, the need to invest in high finishing techniques is essential to improve the integrity of the models.
Color printing: BJ easily allows multicolored construction within a single layer. Additionally, the use of water-based inks reduces the cost of these color prints when compared to other AM material blasting techniques. Such feature makes BJ attractive for the construction of visualization models for architecture and medicine, for instance.	**Materials:** compared to other 3D printing technologies, the variety of materials available is small.
Authors' comments: on the color 3D printing, it should be noted that the similarity with the 2D printing is evident by the composition of colors (base colors mixtures) and by the transposition of what could be a picture on paper to a three-dimensional model. The management of the technology is also accessible to the user (user-friendly), without the need for large parametric configurations and easy insertion of the print file in the manufacturing machine.	**Authors' comments:** thinking about our equipment context (CJP), BJ loses a lot of space in the production of models within the scope of academic research and functional component developed by our students. Competition with extrusion-based 3D printing (FFF) is nearly impossible. The large equipment makes it difficult to use as a teaching tool. In addition, compared to FFF, consumable costs make continuous parts production unviable. Finally, posttreatment that involves resins releases strong odors and often contributes to the formation of dirt in the environment.

10.3 Technology applications

Multicolored 3D printing is in fact one of the great attractions of BJ technology. This characteristic is the pillar of one of its main applications, the construction of elements for visualization. Reproducing the colors of the models in detail is a highly attractive element in the representation of parts and prototypes for the toy industries, appliances, models, fashion, or for the medical field in the development of studies on anatomy, diseases, injuries, and assistive devices, among others [1,29–34] (Figs. 10.4–10.6). Another sector that benefits from this attribute is the production of personalized items such as busts, figurines obtained by 3D scanning, trophies, and others (Figs. 10.7–10.9).

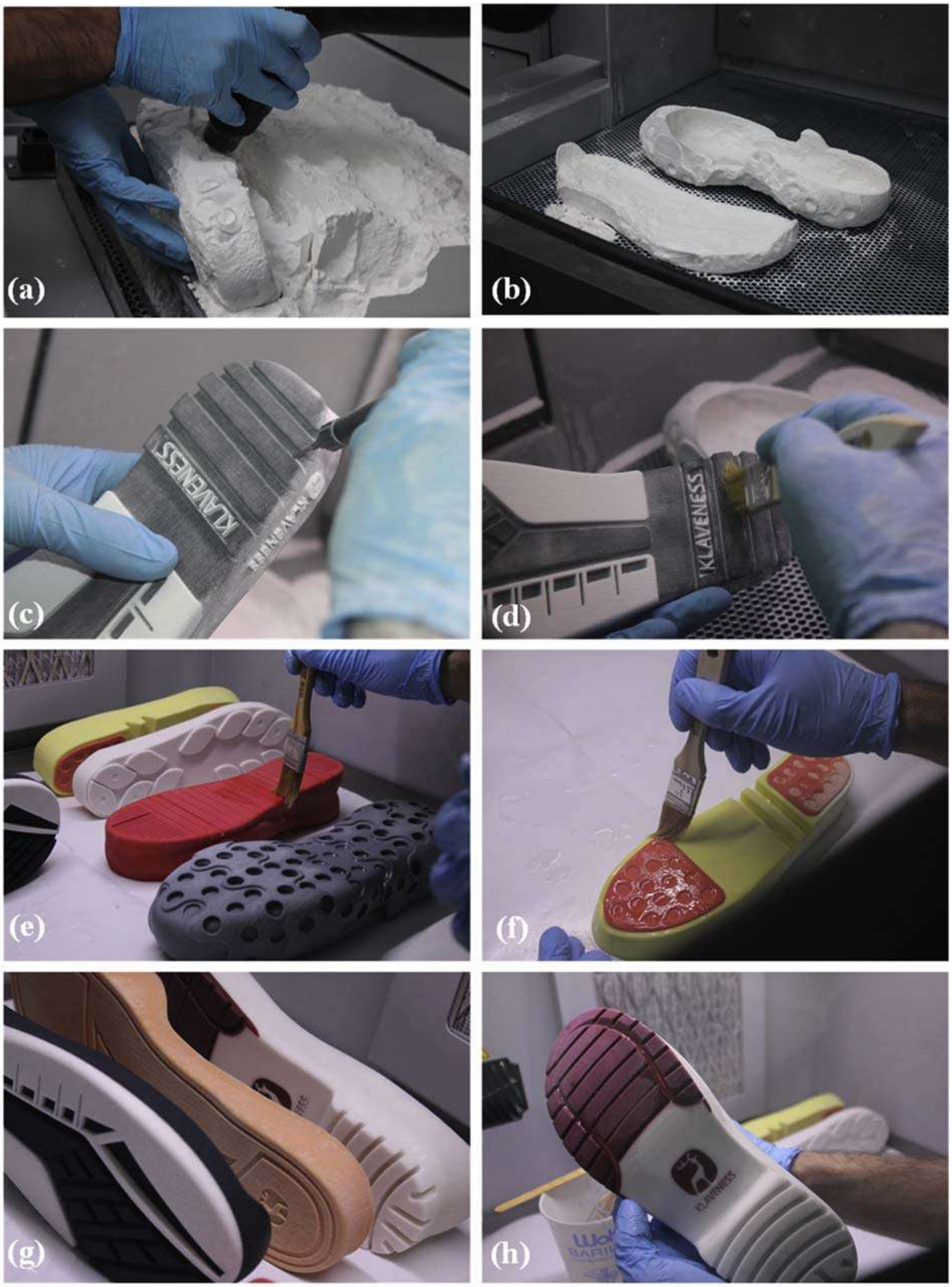

FIGURE 10.4 Development of different concepts of shoe soles by BJ: removal of the piece and unused powder (A) and (B), cleaning of the piece (C) and (D), application of infiltrant (E) and (F), and final parts (G) and (H). (Source: *courtesy of Professors Jorge Lino and Lígia Lopes and Doctor Isaac Ferreira).*

FIGURE 10.5 Printed medical model: pelvic bones (A) and internal organs (B) and (C). (Source: *courtesy of Professors Jorge Lino and Augusto Fernandes).*

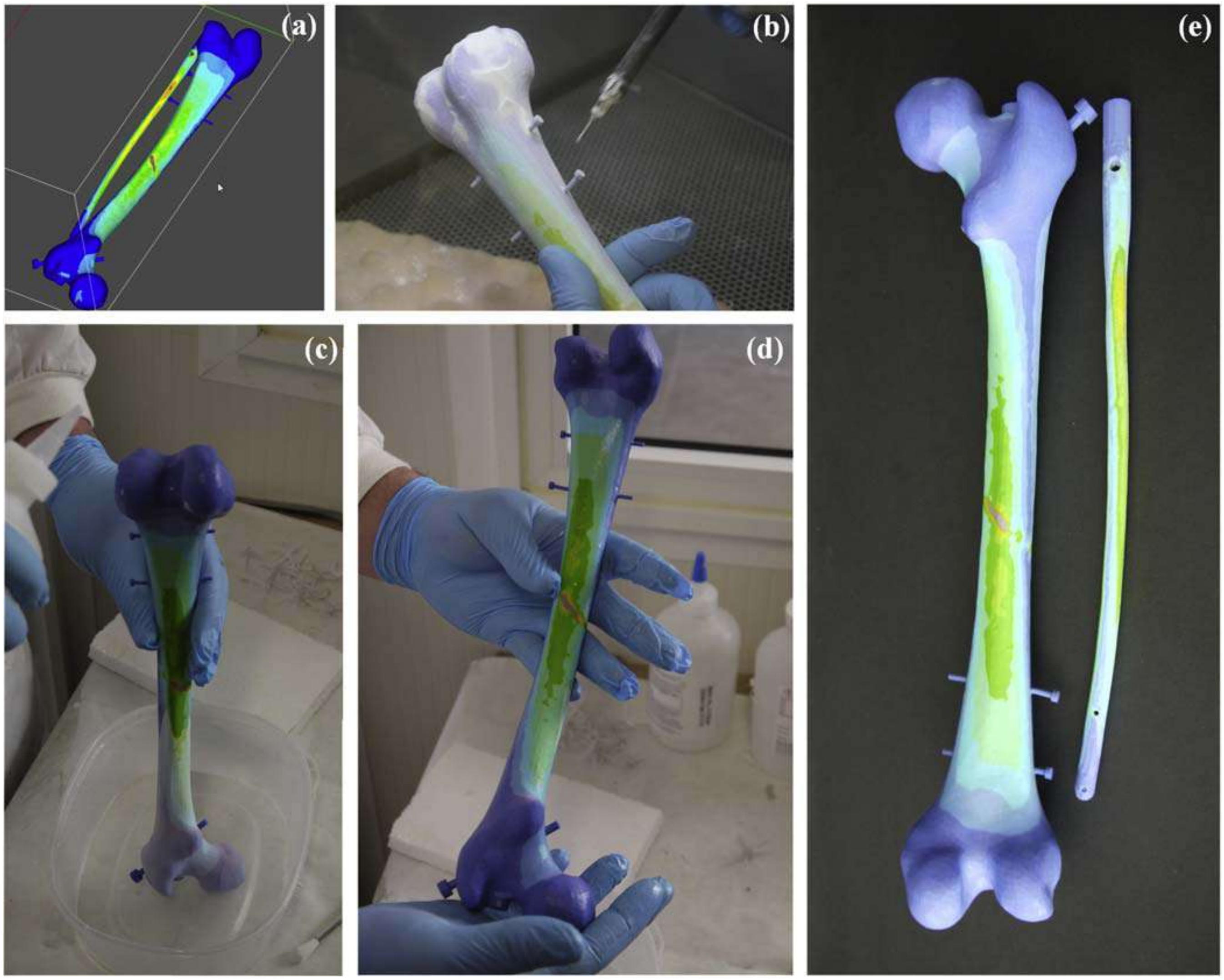

FIGURE 10.6 BJ printing of a bone model and implant with colors resulting from simulation analysis: virtual model (A), cleaning of the printed part (B), application of cyanoacrylate (C) and (D), and final parts (E). (Source: *courtesy of Doctor Maria Goreti Fernandes).*

FIGURE 10.7 3D printing of custom figurine: 3D scanning (A) and (B), cleaning of the model (C), part after application of cyanoacrylate (D), and Professor Lino and his statues (E). (Source: *courtesy of Professor Jorge Lino and Tridaxis).*

Considering the universe of available materials, other applications of BJ printing are related to its use in the construction of scaffolds, pharmaceutical devices, food industry, mold making (sand, silicone), tooling (metal), metallic foam structures, etc. [1,3,4,24,35–45]. Among the aforementioned applications, the use of BJ technology in making sand molds is an important highlight in the scientific field, with numerous publications on the subject in recent years. Together with the Selective Laser Sintering (SLS) and Patternless Casting Manufacturing (PCM) techniques, BJ is one of the most used for this scenario [46].

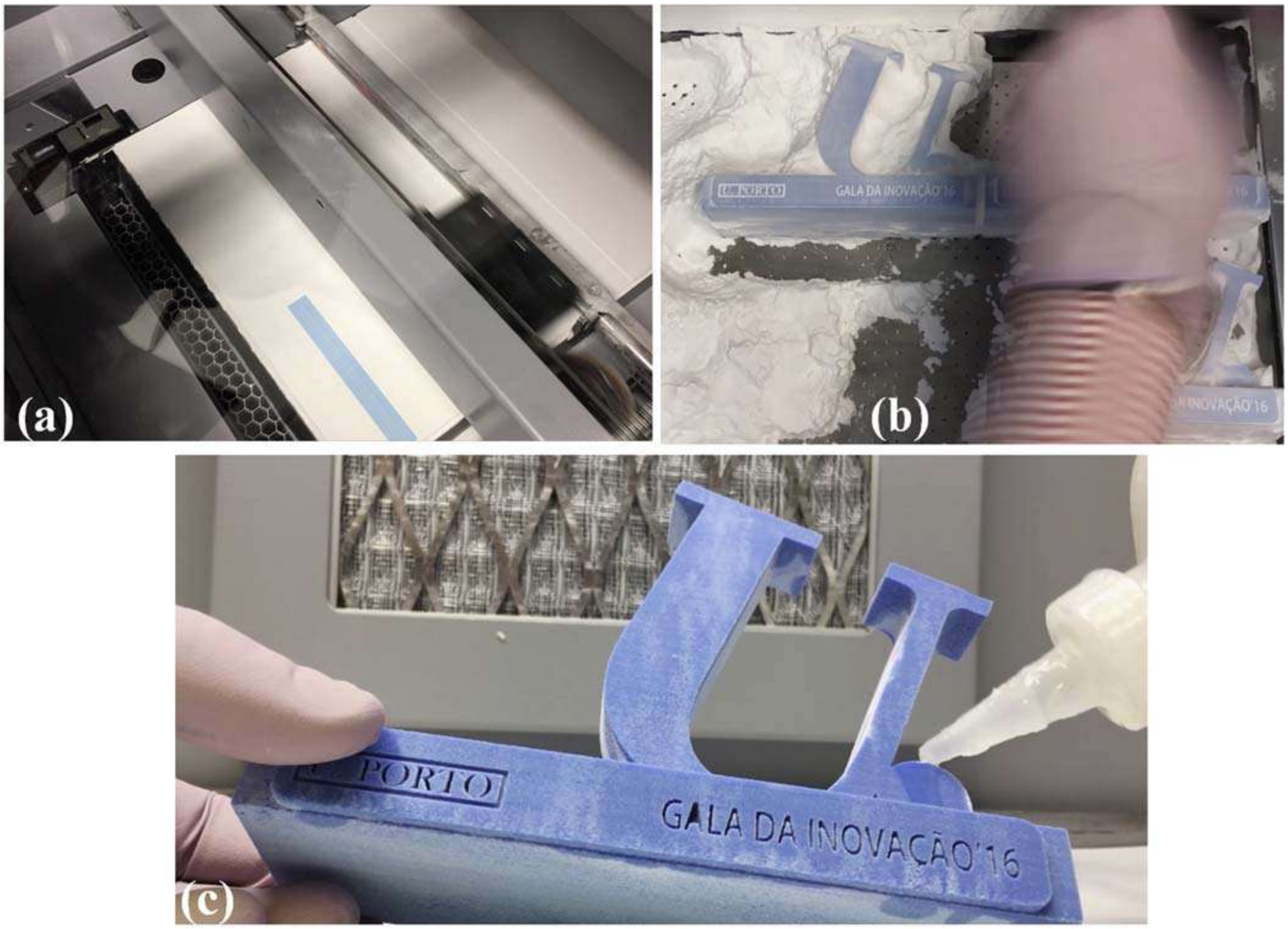

FIGURE 10.8 BJ printing of the trophy for the "Innovation Gala" award: printing of the part (A), cleaning (B), and application of cyanoacrylate (C). (Source: *courtesy of Professor Jorge Lino and Rectory of University of Porto).*

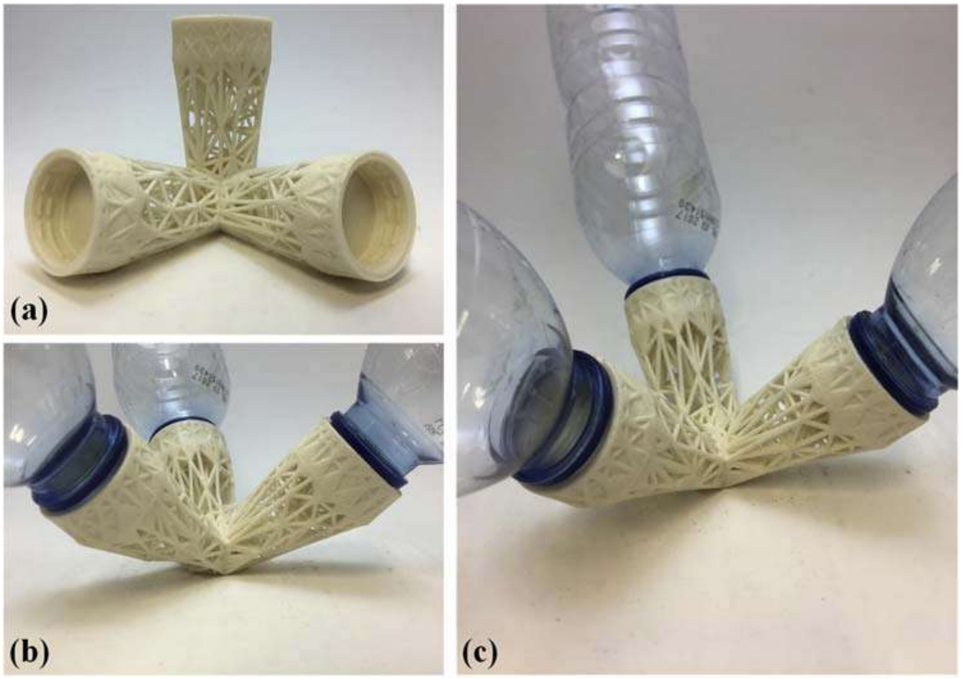

FIGURE 10.9 Spices organizer: (A) printed model and assembled bottles (B) and (C). (Source: *courtesy of Professor Jorge Lino).*

Hawaldar and Zhang [47] compared the construction of sand molds obtained by BJ printing and the conventional manufacturing technique. According to the authors, if considered a small-scale mold production, the AM process is more effective than the traditional method in terms of sand and metal savings used, design allowances, and fettling work. In addition, they highlight even better surface finish and dimensional quality of the printed molds. However, the authors warn of the higher costs associated with 3D printing.

Hackney and Wooldridge [48] also point out that the use of 3D printing is interesting in obtaining sand molds, since unlike the traditional system, it makes possible to build the cavities of the elements without the need for a pattern (a form of the final product), thus reducing the times involved in the process. They used BJ technology to print a mold for casting aluminum turbochargers. Other recent research in this area has been carried out to assess the mechanical strength of the molds, their permeability, and microstructural characteristics [49,50].

10.4 Binder Jetting machines

The leading companies in the market, 3D Systems™, ExOne™, and Voxeljet™ present a series of equipment available on their commercial pages, which, due to their great capabilities, are restricted to a specific audience. In this sense, due to our maker nature, we chose to present here some initiatives in the scope of the popularization of the BJ technology.

One of the precursors in this scenario was the "Pwdr Model 0.1" 3D printer, developed by researchers at the University of Twente (Netherlands). It is an open-source system that allows the construction of parts both by the BJ process and by the SLS technology, with minimal modifications. When configured in the BJ technique, the machine can operate with plaster powders, ceramics, concrete, and sugar, among others. The device features specifications such as: maximum print size (125 × 125 × 125) mm, 96 DPI printhead resolution, and a 50 μm vertical axis increment [51]. The presentation of the concept as well as analysis of it printing with ceramics are carried out in Budding, Vaneker, and Winnubst study [52]. Other movements in the development of equipment in the academic/scientific scenario are observed in Dixon's [53] and Kindblom et al. [54] studies. Simões et al. [55] also worked on the concept of a machine for printing parts from fine wood powder resulting from machining process.

Another example is the "Plan B" project. Developed by the Dutch engineer Yvo de Haas, the equipment is simple and consists of an electronics common to open-source 3D printers (extrusion-based), components of conventional inkjet printers, in addition to a structure composed of aluminum, and elements printed by FFF (Fused Filament Fabrication). Its working volume is approximately (150 × 150 × 100) mm, with an ink injector with 96 DPI resolution and printing capacity with layer thicknesses between 0.1 and 0.25 mm. The parts obtained by these machines are built in plaster powders and then subjected to treatment with epoxy resins, cyanoacrylate, or waxes [56]. Interested parties can consult the "step by step" for the construction of the printer on the Ytec3D website [57].

The last example of an open-source BJ system was presented by the same Yvo de Hass in his participation in the Hackaday Award 2018, the so-called Oasis 3DP printer. It is described as capable of working with plaster, ceramics, sand, sugar, and metal. Technically, it has a printing area with 84 mm diameter and 100 mm height. The binder deposit is made by a system with 600 DPI resolution [58,59]. Information about the project is available on the Hackaday.io platform [59].

10.5 Binder Jetting 3D printing and polymers materials

The amount of specific information about the polymeric materials in the BJ process is less than that generally found for other AM technologies, both in scientific and technical literature. This view is also supported in the recent work, respectively, 2019 and 2020, by Ziaee and Crane [39] and Wang et al. [60]. For Ziaee and Crane [39], a justification for this, in the case of powders, is that polymers are rarely manufactured from this state and, therefore, few formulations are available.

Another reason may be associated with the fact that the BJ technique is formed largely by closed systems, mainly in terms of equipment and materials. This characteristic, in a way, restrains research, as it makes it difficult for the "curious" to easily vary the input materials of the process, whether they are powders or binders. The raw materials used in these systems are even presented to the public with commercial names and with protections on their formulation, so, many times, we do not even know if the polymers are inserted or not. This is perfectly understandable when the market wants a “plug and play” product, whose objective is results with little need for investigations into causes and effects.

Despite the low demand, we try to present here some initiatives of powders, binders, and infiltrants within the polymers scope. Note that the use of PMMA, powder, by Voxeljet™ in its printers was mentioned at the beginning of this chapter, which can be considered a good “sign of life” of polymers in the context of BJ. Studies from the 1990s, such as those by Wu et al. [61] and Giordano et al. [62], show the application of poly(ε-caprolactone) (PCL), poly(ethylene oxide) (PEO), and poly(lactic acid) (PLA) powders in the construction and analysis of parts for applications in the medical environment. PLA powder is also used in Huang et al. [63] study in the production of implants for controlled drug administration. Lam et al. [64] printed scaffolds using a mixture of corn starch (polysaccharide composed of two polymers, amylase and amylopectin), dextran (polysaccharide), and gelatin (collagen obtained from animals).

In the construction of piezoelectric scaffolds, Polley et al. [42] added the composition of barium-titanium powder and hydroxyapatite ($BaTiO_3$/HA) to a polymeric component of poly(ethyl methacrylate) (PEMA). Suwanprateeb and Chumnanklang [65] worked on the construction of porous structures using a mixture of high-density polyethylene (HDPE) with maltodextrin as base material. In another study, Suwanprateeb et al. [66] evaluated a combination of HDPE with maltodextrin and poly(vinyl alcohol) (PVA) to be used in bone implants.

Other powders based on silicones [67], mixtures of graphite and Nylon-12 [68], or dental plaster with hydroxypropyl methylcellulose − reinforced, for example, with polyacrylonitrile (PAN) or polyamide (PA) fibers [69] − in addition to food materials such as cellulose [44], are also references in the scientific literature of polymers in the BJ printing. In the commercial scenario, the recent developments of the German company Evonik™ stand out, such as the production of PEBA (polyether block amide) elastomeric (flexible) powder, suitable for BJ, SLS, and high-speed sintering (HSS) techniques [70].

Polymers such as poly(vinylpyrrolidone) (PVP), polyacrylamide (PAM), and poly(vinyl alcohol) (PVA) were used as binders in the studies of Chai et al. [71] and Wei et al. [72] in BJ with hydroxyapatite (powder). PVP, as binder, is also used in Wilts et al. [73]. Huang et al. [74], in turn, present a silicate binder modified with butyl acrylate (BA) and polyacrylamide (PAM). Gilmer et al. [75] use the monomer triethylene glycol dimethacrylate (TEG-DMA) in the BJ process with metals.

Finally, the infiltrating materials: the most used polymers are cyanoacrylate and epoxy resins [7,36,76−81]; however, elements such as polycarbosilane [82] are also mentioned.

10.6 Final considerations

The BJ technology is a simple way of translating the concept of 3D printing to a layman, largely because of the equipment’s characteristics and its multicolor printing capacity. However, a number of limitations need to be overcome so that the BJ concept does not get obsolete because of the development of similar powder processing technologies, such as Voxeljet™ High Speed Sintering (HSS) [83] and HP™ Multi Jet Fusion [84]. They differ from BJ in that the process produces the final properties directly from the machine rather than a green part [39].

One of the solutions to this problem would be its affirmation between academics and enthusiasts through open-source systems. In other words, these “machines” need a revolution similar to what happened with extrusion-based AM. The basic projects in that context, such as RepRap and Fab@home, were key for the development of Fused Filament Fabrication (FFF), allowing different views, technical or not, to be used to improve the quality of machines and parts.

Following these movements, many companies offered desktop equipment, and later there was a significant growth in the range of building materials available. At the same time, there was a decrease in costs. This new scenario provided a strengthening of the use of extrusion-based AM in final products. This path is a prerequisite for the future of BJ 3D Printing.

Several minds coming together would ease the process of overcoming limitations of BJ such as the low mechanical strength of the parts, as well as the time spent on posttreatments, thus allowing the expansion and support of the technology for other scenarios. Despite the recommendations on accessibility and development issues, it was possible to observe, in a general overview, that research on BJ in the last year, and the beginning of the present, points to questions on ceramics and metals.

References

[1] N. Volpato, A.L.J. Munhoz, C.A. Costa, C.H. Ahrens, J. De Carvalho, J.R.L. Dos Santos, J.V.L. Da Silva, J.A. Foggiatto, M.S.F. De Lima, Manufatura Aditiva: Tecnologias e aplicações da impressão 3D, first ed., Blucher, São Paulo, 2017.

[2] S. Pollack, C. Venkatesh, M. Neff, A.V. Healy, G. Hu, E.A. Fuenmayor, J.G. Lyons, I. Major, D.M. Devine, Polymer-based additive manufacturing: historical developments, process types and material considerations, in: D.M. Devine (Ed.), Polymer-Based Additive Manufacturing: Biomedical Applications, Springer International Publishing, Cham, 2019, pp. 1–22, https://doi.org/10.1007/978-3-030-24532-0_1.

[3] I. Gibson, D. Rosen, B. Stucker, Additive Manufacturing Technologies: 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing, Second ed., Springer New York, New York, NY, 2015 https://doi.org/10.1007/978-1-4939-2113-3.

[4] Z. Rahman, N.A. Charoo, M. Kuttolamadom, A. Asadi, M.A. Khan, Printing of personalized medication using binder jetting 3D printer, in: J. Faintuch, S. Faintuch (Eds.), Precision Medicine for Investigators, Practitioners and Providers, Elsevier, 2020, pp. 473–481, https://doi.org/10.1016/B978-0-12-819178-1.00046-0.

[5] Y. Zhang, W. Jarosinski, Y.-G. Jung, J. Zhang, Additive manufacturing processes and equipment, in: J. Zhang, Y.-G. Jung (Eds.), Additive Manufacturing: Materials, Processes, Quantifications and Applications, Elsevier, 2018, pp. 39–51, https://doi.org/10.1016/B978-0-12-812155-9.00002-5.

[6] F.J.L. Alves, F.J.S. Braga, M.S. Simão, R.J. de L. Neto, T.M.G.P. Duarte, Protoclick! Prototipagem Rápida, first ed., Protoclick, Leça do Balio, 2001.

[7] T.J. Ayres, S.R. Sama, S.B. Joshi, G.P. Manogharan, Influence of resin infiltrants on mechanical and thermal performance in plaster binder jetting additive manufacturing, Addit. Manuf. 30 (2019) 100885, https://doi.org/10.1016/j.addma.2019.100885.

[8] J. Yuan, M. Zhu, B. Xu, G. Chen, Review on processes and color quality evaluation of color 3D printing, Rapid Prototyp. J. 24 (2018) 409–415, https://doi.org/10.1108/RPJ-11-2016-0182.

[9] M. Stanic, B. Lozo, D. Gregor Svetec, Colorimetric properties and stability of 3D prints, Rapid Prototyp. J. 18 (2012) 120–128, https://doi.org/10.1108/13552541211212104.

[10] E. Ocaña-Garzón, J.L. Alves, Mechanical properties of bending 3DP models of different thickness infiltrated with alternative materials, Int. J. Adv. Eng. Technol. 3 (2019) 27–37. http://www.newengineeringjournal.com/search/Mechanical properties of bending 3DP models of different thickness infiltrated with alternative materials.

[11] ExOne, Metal 3D Printers – Materials & Binders, 2020. https://www.exone.com/en-US/3d-printing-materials-and-binders/metal-materials-binders (Accessed 5 May 2020).

[12] ExOne, ExOne Metal Binder Jet 3D Printing Process, 2020. https://www.youtube.com/watch?v=mESROjEysSw (Accessed 5 May 2020).

[13] Voxeljet, Voxeljet Services, 2018, p. 6. https://www.voxeljet.com/fileadmin/user_upload/PDFs/Servicebrochure_2018_web_01.pdf.

[14] Voxeljet, Voxeljet – The 3D Printing Process, 2018. https://www.youtube.com/watch?v=hjIoGPZPNjU (Accessed 5 May 2020).

[15] S.R. Sama, T. Badamo, P. Lynch, G. Manogharan, Novel sprue designs in metal casting via 3D sand-printing, Addit. Manuf. 25 (2019) 563–578, https://doi.org/10.1016/j.addma.2018.12.009.

[16] T.A. Le Néel, P. Mognol, J.-Y. Hascoët, A review on additive manufacturing of sand molds by binder jetting and selective laser sintering, Rapid Prototyp. J. 24 (2018) 1325–1336, https://doi.org/10.1108/RPJ-10-2016-0161.

[17] EnvisionTEC, Viridis3D – Robotic Additive Manufacturing, 2016. https://www.youtube.com/watch?v=lacCTzU3wsk (Accessed 23 June 2020).

[18] D. Mitterberge, T. Derme, Soil 3D printing, in: K. Bieg, D. Briscoe, C. Odom (Eds.), Proceedings of the 39th Annual Conference of the Association for Computer Aided Design in Architecture, Association for Computer Aided Design in Architecture (ACADIA), 2019, pp. 585–595. http://papers.cumincad.org/data/works/att/acadia19_586.pdf.

[19] A. Della Bona, P.H. Corazza, Y. Zhang, Characterization of a polymer-infiltrated ceramic-network material, Dent. Mater. 30 (2014) 564–569, https://doi.org/10.1016/j.dental.2014.02.019.

[20] A. Mostafaei, A.M. Elliott, J.E. Barnes, C.L. Cramer, P. Nandwana, M. Chmielus, Binder jet 3D printing – process parameters, materials, properties, and challenges, Prog. Mater. Sci. (2020) 100684, https://doi.org/10.1016/j.pmatsci.2020.100684.

[21] Y. Bai, C.B. Williams, An exploration of binder jetting of copper, Rapid Prototyp. J. 21 (2015) 177–185, https://doi.org/10.1108/RPJ-12-2014-0180.

[22] D. Günther, F. Mögele, Additive manufacturing of casting tools using powder-binder- jetting technology, in: New Trends 3D Print, InTech, 2016, https://doi.org/10.5772/62532.

[23] R. Vaidyanathan, Additive manufacturing technologies for polymers and composites, in: A. Bandyopadhyay, S. Bose (Eds.), Additive Manufacturing, CRC Press Taylor & Francis Group, Boca Raton, FL, 2016, pp. 19–64.

[24] B. Redwood, F. Schöffer, B. Garret, The 3D Printing Handbook: Technologies, Design and Applications, 3D Hubs B. V., Amsterdam, 2017.

[25] P.K. Gokuldoss, S. Kolla, J. Eckert, Additive manufacturing processes: selective laser melting, electron beam melting and binder jetting—selection guidelines, Materials 10 (2017) 672, https://doi.org/10.3390/ma10060672.

[26] S.C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, Polymers for 3D printing and customized additive manufacturing, Chem. Rev. 117 (2017) 10212–10290, https://doi.org/10.1021/acs.chemrev.7b00074.

[27] H. Miyanaji, Binder Jetting Additive Manufacturing Process Fundamentals and the Resultant Influences on Part Quality, University of Louisville, 2018, https://doi.org/10.18297/etd/3058.

[28] L. Gregurić, What Is Binder Jetting? – 3D Printing Simply Explained, 2019. https://all3dp.com/2/what-is-binder-jetting-3d-printing-simply-explained/ (Accessed 8 May 2020).

[29] J.L. Alves, L. Lopes, A.D. Meneses, Utilização das tecnologias de fabrico aditivo no desenvolvimento de sapatos para pessoas com paralisia cerebral, Rev. Robótica. (2015) 78–81.

[30] A. Vanderploeg, S.-E. Lee, M. Mamp, The application of 3D printing technology in the fashion industry, Int. J. Fash. Des. Technol. Educ. 10 (2017) 170–179, https://doi.org/10.1080/17543266.2016.1223355.

[31] M.Y. Chen, J. Skewes, M. Desselle, C. Wong, M.A. Woodruff, P. Dasgupta, N.J. Rukin, Current applications of three-dimensional printing in urology, BJU Int. 125 (2020) 17–27, https://doi.org/10.1111/bju.14928.

[32] M. Salmi, Possibilities of preoperative medical models made by 3D printing or additive manufacturing, J. Med. Eng. 2016 (2016) 1−6, https://doi.org/10.1155/2016/6191526.

[33] A.D. Meneses, J.L. Alves, L. Lopes, Study of 3D printing potential in supporting the manufacturing process of shoes for people with cerebral palsy, Int. J. Mater. Eng. Innovat. 7 (2016) 184−199. http://www.inderscience.com/offer.php?id=84622.

[34] M.G. Fernandes, J.L. Alves, E.M.M. Fonseca, Diaphyseal femoral fracture: 3D biomodel and intramedullary nail created by additive manufacturing, Int. J. Mater. Eng. Innovat. 7 (2016) 130−142. http://www.inderscience.com/offer.php?id=79556.

[35] S. Mitra, Experimental and Numerical Characterization of Functional Properties of Sand Molds Produced by Additive Manufacturing (3D Printing by Jet Binding) in a Fast Foundr, Hesam Université, 2019.

[36] M. Maravola, B. Conner, J. Walker, P. Cortes, Epoxy infiltrated 3D printed ceramics for composite tooling applications, Addit. Manuf. 25 (2019) 59−63, https://doi.org/10.1016/j.addma.2018.10.036.

[37] H. Miyanaji, D. Ma, M.A. Atwater, K.A. Darling, V.H. Hammond, C.B. Williams, Binder jetting additive manufacturing of copper foam structures, Addit. Manuf. 32 (2020) 100960, https://doi.org/10.1016/j.addma.2019.100960.

[38] D.A. Snelling, C.B. Williams, A.P. Druschitz, Mechanical and material properties of castings produced via 3D printed molds, Addit. Manuf. 27 (2019) 199−207, https://doi.org/10.1016/j.addma.2019.03.004.

[39] M. Ziaee, N.B. Crane, Binder jetting: a review of process, materials, and methods, Addit. Manuf. 28 (2019) 781−801, https://doi.org/10.1016/j.addma.2019.05.031.

[40] P. Tian, F. Yang, L.-P. Yu, M.-M. Lin, W. Lin, Q.-F. Lin, Z.-F. Lv, S.-Y. Huang, Y.-Z. Chen, Applications of excipients in the field of 3D printed pharmaceuticals, Drug Dev. Ind. Pharm. 45 (2019) 905−913, https://doi.org/10.1080/03639045.2019.1576723.

[41] F. Chinellato, J. Wilbig, D. Al-Sabbagh, P. Colombo, J. Günster, Gas flow assisted powder deposition for enhanced flowability of fine powders: 3D printing of α-tricalcium phosphate, Open Ceram. 1 (2020) 100003, https://doi.org/10.1016/j.oceram.2020.100003.

[42] C. Polley, T. Distler, R. Detsch, H. Lund, A. Springer, A.R. Boccaccini, H. Seitz, 3D printing of piezoelectric barium titanate-hydroxyapatite scaffolds with interconnected porosity for bone tissue engineering, Materials 13 (2020) 1773, https://doi.org/10.3390/ma13071773.

[43] S. Holland, C. Tuck, T. Foster, Selective recrystallization of cellulose composite powders and microstructure creation through 3D binder jetting, Carbohydr. Polym. 200 (2018) 229−238, https://doi.org/10.1016/j.carbpol.2018.07.064.

[44] S. Holland, T. Foster, W. MacNaughtan, C. Tuck, Design and characterisation of food grade powders and inks for microstructure control using 3D printing, J. Food Eng. 220 (2018) 12−19, https://doi.org/10.1016/j.jfoodeng.2017.06.008.

[45] S. Holland, T. Foster, C. Tuck, Creation of food structures through binder jetting, in: F.C. Godoi, B.R. Bhandari, S. Prakash, M. Zhang (Eds.), Fundamentals of 3D Food Printing and Applications, Elsevier, 2019, pp. 257−288, https://doi.org/10.1016/B978-0-12-814564-7.00009-2.

[46] D. Zhao, W. Guo, B. Zhang, F. Gao, 3D sand mould printing: a review and a new approach, Rapid Prototyp. J. 24 (2018) 285−300, https://doi.org/10.1108/RPJ-05-2016-0088.

[47] N. Hawaldar, J. Zhang, A comparative study of fabrication of sand casting mold using additive manufacturing and conventional process, Int. J. Adv. Manuf. Technol. 97 (2018) 1037−1045, https://doi.org/10.1007/s00170-018-2020-z.

[48] P. Hackney, R. Wooldridge, Optimisation of additive manufactured sand printed mould material for aluminium castings, Procedia Manuf. 11 (2017) 457−465, https://doi.org/10.1016/j.promfg.2017.07.136.

[49] T. Sivarupan, M. El Mansori, N. Coniglio, M. Dargusch, Effect of process parameters on flexure strength and gas permeability of 3D printed sand molds, J. Manuf. Process. 54 (2020) 420−437, https://doi.org/10.1016/j.jmapro.2020.02.043.

[50] S. Mitra, M. EL Mansori, A. Rodríguez de Castro, M. Costin, Study of the evolution of transport properties induced by additive processing sand mold using X-ray computed tomography, J. Mater. Process. Technol. 277 (2020) 116495, https://doi.org/10.1016/j.jmatprotec.2019.116495.

[51] 3ders.org, First Open Source Powder-Based 3D Printer, 2012. https://www.3ders.org/articles/20120803-first-open-source-powder-based-3d-printer.html (Accessed 12 June 2020).

[52] A. Budding, T.H.J. Vaneker, A.J.A. Winnubst, Open source powder based rapid prototyping machine for ceramics, Procedia CIRP 6 (2013) 533−538, https://doi.org/10.1016/j.procir.2013.03.101.

[53] B. Dixon, Development of Low Cost Inkjet 3D Printing for the Automotive Industry, Massey University, 2017. https://mro.massey.ac.nz/bitstream/handle/10179/12797/02_whole.pdf?sequence=2&isAllowed=y.

[54] M. Kindblom, R. Abdeljawad, S.A. Mohammadi, Construction of a Powder Bed 3D Printer, 2018, p. 38. http://uu.diva-portal.org/smash/record.jsf?pid=diva2%3A1235702&dswid=-5489.

[55] R.P. Simões, F.J. Lino, R.J.L. Neto, Application of wood powder to produce prototypes using the principles of additive manufacturing, in: Materiais 2007, Porto, 2007.

[56] 3ders.org, Plan B Is an Open Source, DIY Powder-Based 3D Printer, 2014. https://www.3ders.org/articles/20140821-plan-b-is-an-open-source-diy-powder-based-3d-printer.html (Accessed 12 June 2020).

[57] Ytec 3D, Building a Plan B. https://ytec3d.com/plan-b-building/ (Accessed 12 May 2020).

[58] C. Scott, The Oasis 3DP Brings Open Source Binder Jetting to Makers, 2018. https://3dprint.com/227079/oasis-3dp-open-source-binder-jetting/ (Accessed 12 June 2020).

[59] Y. de Haas, Oasis 3DP: A Powder and Inkjet 3D Printer Based on HP45 Inkjet Technology, Hackaday.Io, 2018. https://hackaday.io/project/86954-oasis-3dp (Accessed 12 May 2020).

[60] Y. Wang, Z. Xu, D. Wu, J. Bai, Current status and prospects of polymer powder 3D printing technologies, Materials 13 (2020) 2406, https://doi.org/10.3390/ma13102406.

[61] B.M. Wu, S.W. Borland, R.A. Giordano, L.G. Cima, E.M. Sachs, M.J. Cima, Solid free-form fabrication of drug delivery devices, J. Contr. Release 40 (1996) 77−87, https://doi.org/10.1016/0168-3659(95)00173-5.

[62] R.A. Giordano, B.M. Wu, S.W. Borland, L.G. Cima, E.M. Sachs, M.J. Cima, Mechanical properties of dense polylactic acid structures fabricated by three dimensional printing, J. Biomater. Sci. Polym. Ed. 8 (1997) 63−75, https://doi.org/10.1163/156856297X00588.

[63] W. Huang, Q. Zheng, W. Sun, H. Xu, X. Yang, Levofloxacin implants with predefined microstructure fabricated by three-dimensional printing technique, Int. J. Pharm. 339 (2007) 33−38, https://doi.org/10.1016/j.ijpharm.2007.02.021.

[64] C.X. Lam, X. Mo, S. Teoh, D. Hutmacher, Scaffold development using 3D printing with a starch-based polymer, Mater. Sci. Eng. C 20 (2002) 49−56, https://doi.org/10.1016/S0928-4931(02)00012-7.

[65] J. Suwanprateeb, R. Chumnanklang, Three-dimensional printing of porous polyethylene structure using water-based binders, J. Biomed. Mater. Res. B Appl. Biomater. 78B (2006) 138–145, https://doi.org/10.1002/jbm.b.30469.

[66] J. Suwanprateeb, S. Kerdsook, T. Boonsiri, P. Pratumpong, Evaluation of heat treatment regimes and their influences on the properties of powder-printed high-density polyethylene bone implant, Polym. Int. 60 (2011) 758–764, https://doi.org/10.1002/pi.3006.

[67] F. Liravi, M. Vlasea, Powder bed binder jetting additive manufacturing of silicone structures, Addit. Manuf. 21 (2018) 112–124, https://doi.org/10.1016/j.addma.2018.02.017.

[68] H. Miyanaji, J.M. Akbar, L. Yang, Fabrication and characterization of Graphite/Nylon 12 composite via binder Jetting additive manufacturing process, in: Proceedings of 28th Annual International Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference, Austin, 2017, pp. 593–604. https://sffsymposium.engr.utexas.edu/sites/default/files/2017/Manuscripts/FabricationandCharacterizationofGraphiteNylon.pdf.

[69] S. Christ, M. Schnabel, E. Vorndran, J. Groll, U. Gbureck, Fiber reinforcement during 3D printing, Mater. Lett. 139 (2015) 165–168, https://doi.org/10.1016/j.matlet.2014.10.065.

[70] T. Boissonneault, Evonik Introduces First Flexible PEBA-Based Powder for 3D Printing, 2018. https://www.3dprintingmedia.network/evonik-peba-based-powder-3d-printing/ (Accessed 11 June 2020).

[71] W. Chai, Q. Wei, M. Yang, K. Ji, Y. Guo, S. Wei, Y. Wang, The printability of three water based polymeric binders and their effects on the properties of 3D printed hydroxyapatite bone scaffold, Ceram. Int. 46 (2020) 6663–6671, https://doi.org/10.1016/j.ceramint.2019.11.154.

[72] Q. Wei, Y. Wang, W. Chai, Y. Zhang, X. Chen, Molecular dynamics simulation and experimental study of the bonding properties of polymer binders in 3D powder printed hydroxyapatite bioceramic bone scaffolds, Ceram. Int. 43 (2017) 13702–13709, https://doi.org/10.1016/j.ceramint.2017.07.082.

[73] E.M. Wilts, D. Ma, Y. Bai, C.B. Williams, T.E. Long, Comparison of linear and 4-arm star poly(vinyl pyrrolidone) for aqueous binder jetting additive manufacturing of personalized dosage tablets, ACS Appl. Mater. Interfaces 11 (2019) 23938–23947, https://doi.org/10.1021/acsami.9b08116.

[74] S.-J. Huang, C.-S. Ye, H.-P. Zhao, Z.-T. Fan, Parameters optimization of binder jetting process using modified silicate as a binder, Mater. Manuf. Process. 35 (2020) 214–220, https://doi.org/10.1080/10426914.2019.1675890.

[75] D. Gilmer, L. Han, E. Hong, D. Siddel, A. Kisliuk, S. Cheng, D. Brunermer, A. Elliott, T. Saito, An in-situ crosslinking binder for binder jet additive manufacturing, Addit. Manuf. 35 (2020) 101341, https://doi.org/10.1016/j.addma.2020.101341.

[76] C.L. Cramer, A.M. Elliott, J.O. Kiggans, B. Haberl, D.C. Anderson, Processing of complex-shaped collimators made via binder jet additive manufacturing of B4C and pressureless melt infiltration of Al, Mater. Des. 180 (2019) 107956, https://doi.org/10.1016/j.matdes.2019.107956.

[77] R. Aslan, O. Turan, Gypsum-based sound absorber produced by 3D printing technology, Appl. Acoust. 161 (2020) 107162, https://doi.org/10.1016/j.apacoust.2019.107162.

[78] B.F. Lizardo, L.M.G. Vieira, J. Carlos Campos Rubio, T.H. Panzera, J.P. Davim, An assessment of thermosetting infiltrate in powder-based composites made by additive manufacturing, J. Compos. Mater. 53 (2019) 873–882, https://doi.org/10.1177/0021998318792296.

[79] D. Movrin, O. Luzanin, V. Guduric, Using statistically designed experiment to optimize vacuum-assisted post-processing of binder jetted specimens, Rapid Prototyp. J. 25 (2019) 653–663, https://doi.org/10.1108/RPJ-07-2018-0177.

[80] E.M.O. Garzón, Alternative Materials Infiltration in 3D Ceramic Models Printed by Binder Jetting: A Feasibility Assessment, Universidade do Porto, 2019. https://repositorio-aberto.up.pt./handle/10216/120983.

[81] E.O. Garzón, J.L. Alves, R.J. Neto, Post-process influence of infiltration on binder jetting technology, in: L.F.M. da Silva (Ed.), Materials Design and Applications, Springer, 2017, pp. 233–255, https://doi.org/10.1007/978-3-319-50784-2_19.

[82] I. Polozov, N. Razumov, D. Masaylo, A. Silin, Y. Lebedeva, A. Popovich, Fabrication of silicon carbide fiber-reinforced silicon carbide matrix composites using binder jetting additive manufacturing from irregularly-shaped and spherical powders, Materials 13 (2020) 1766, https://doi.org/10.3390/ma13071766.

[83] Voxeljet, Voxeljet High Speed Sintering (HSS) Process, 2017. https://www.youtube.com/watch?v=2jiPUORBu8Q (Accessed 19 May 2020).

[84] HP, HP Multi Jet Fusion Technology's Multi-Agent and Multi-Pass Printing Process | 3D Printing | HP, 2020. https://www.youtube.com/watch?time_continue=15&v=tdNjlmNaNuU&feature=emb_logo (Accessed 19 May 2020).

CHAPTER

11

Sheet lamination

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11.1 Introduction

The process of sheet lamination (SHL), formerly known as laminated object manufacturing (LOM), was developed in 1985 at firm *Helisys*, US, after 2000 known as *Cubic Technologies*. By this process, the products are made by laminating and cutting materials (by laser, knife, CNC machining, etc.) made of paper, polymer films and foils, ceramics, composites, textiles, and metal plates. The plates are laminated into solid blocks by bonding: thermal bonding, adhesive, clamping, ultrasonic, or diffusion welding. For example, for biomedical application thermal bonding is preferable because adhesives may be biologically toxic [1–4].

Applying adhesives, heat, and pressure, each plate, foil, or film fuses into a block and forms a new layer. The material is supplied with a roller on one side of the machine and unwound to the other side (Fig. 11.1). The heated roller provides the pressure and heat required to adhere the new layer to the already made part of the product. The adhesive is activated usually at temperature 60–80°C and a pressure of 10–30 MPa. The working platform is lowered for the thickness of the new layer, which is usually 0.05–0.5 mm [1–3].

Engineering materials can be utilized using this process in combination with a heated bed as if the local temperature of the bed or roller is not controlled well enough, the part may delaminate due to insufficient bonding between layers, or the part may suffer structural damage if the temperatures do not enable good adhesion [4].

After the layer has connected to the previous, the blade or laser beam cuts out contour of the material to form the final product. Typically, a 25 or 50 W CO_2 laser is used. After each cut is completed, the platform lowers by a depth equal to the sheet thickness and another sheet is pulled on top of the previously deposited layers. After a layer is cut, the extra material remains in place to support the part during printing. Support structure is usually cut in shape of cubes for easier separation of product [5–7]. All these steps are presented in Fig. 11.2.

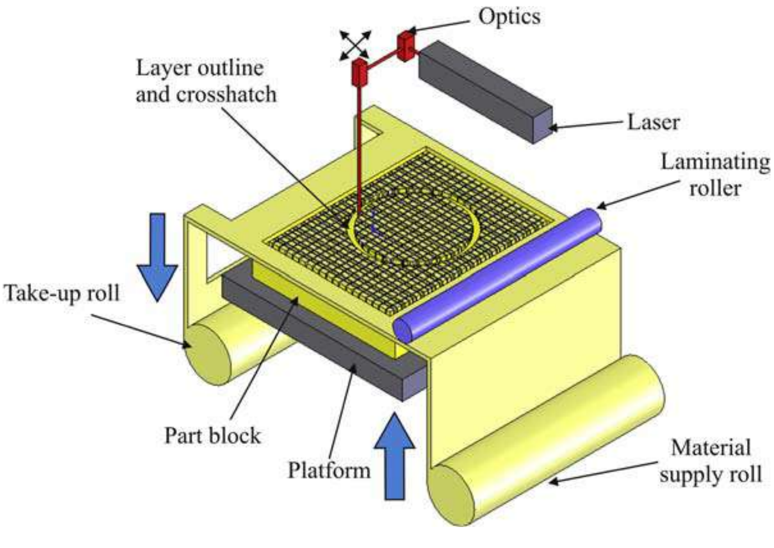

FIGURE 11.1 Process of sheet lamination (SHL) [3]. *Reprinted from [3], Sheet lamination processes, Copyright (2010), with permission from Springer.*

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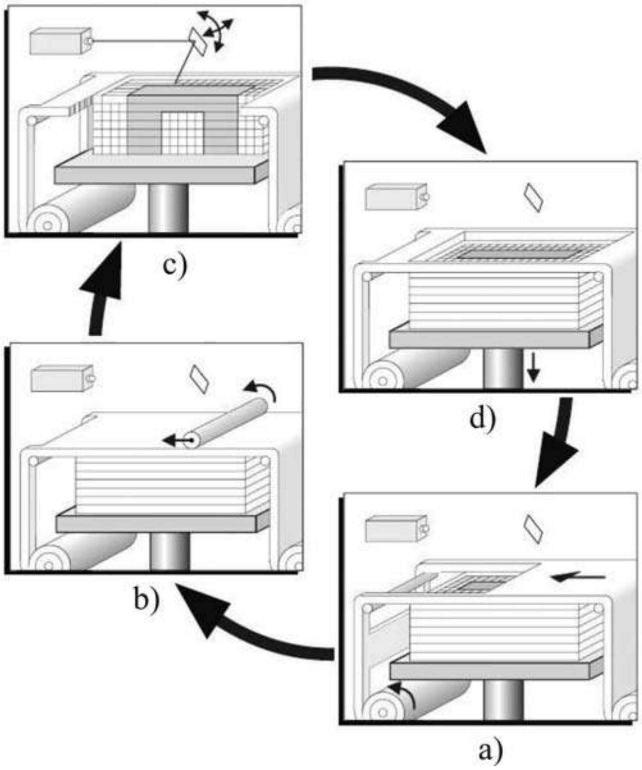

FIGURE 11.2 Steps of sheet lamination: (A) placing a layer of sheet on working platform, (B) joining layers with a heated roller, adhesives, or pressure, (C) cutting of a contour of the product and supporting material into cubes, (D) lowering the platform for production of next layer [8]. *Reprinted from [8], Copyright (2012), with permission from Carl Hanser Verlag.*

11.2 Sheet lamination systems

With the introduction of the SHL process, from 2000 till today, there are a couple of versions of the SHL process, but they all have the same basis, and the difference is in the material that is joined layer by layer and the way that layers are joined. The next section will describe some variants of the SHL procedure.

11.2.1 *Selective deposition lamination*

One laminating-based system, known as selective deposition lamination (SDL), uses paper and is capable of printing in more than 1 million colors. Before 3D printing stacks of standard papers, each precolor-printed is loaded into the feeding tray. The color is usually only on the outer contour for color savings, as it is not usually necessary for the entire cross section to be colored. This process is done with a "regular" printer, but the color penetrates the entire thickness of the paper. This cross section is then cut with blade. In SDL process adhesive (standard glue – polyvinyl acetate (PVA)) is selectively applied to the first sheet of paper. Instead of gluing the whole layer, SDL deposits a higher density of adhesive in the area that will become the product, and a lower density of adhesive in the surrounding area that will function as support. This is because glue tends to blister the paper so a specific coating system based on micro drops was design to overcome this problem. A new sheet of paper is fed from the paper feed mechanism on top of the freshly applied adhesive. The build plate is shifted up to a heating plate and pressure is applied. After the build plate returns to its initial position, an adjustable tungsten-carbide blade cuts the products outline to create the edges of the part (Fig. 11.3) [8–13]. The unused paper (cut in shape of cubes) breaks easily when 3D printing is done, but is still rigid enough to be used as support material (Fig. 11.4) [14].

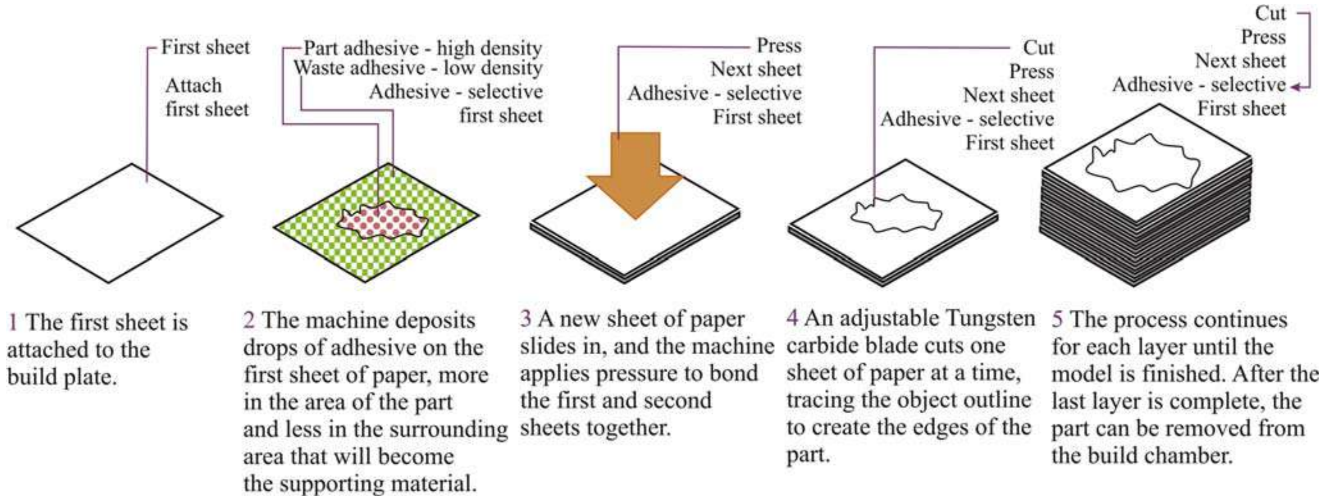

FIGURE 11.3 Process of selective deposition lamination (SDL) [14]. (Source: *courtesy of D. Herzberg).*

FIGURE 11.4 Process of removing support structure in the SDL [14]. (Source: *courtesy of D. Herzberg).*

This process was commercialized by *Mcor Technologies*, Ireland.

Once the SDL process is complete, the products need to be postprocessed, i.e., coating is applied to the surface to achieve better paper properties, primarily strength and elasticity. Because paper is 70% porous, flexibility is achieved with specially formulated water-based PVA coating. Paper objects are usually sealed with a paint or lacquer to keep out moisture. Fig. 11.5 shows the products made by the SDL process with paper.

After the development of the office-friendly, full color, and low-cost *ArkePro* 3D printer, the *Mcor Technologies* was closed and *CleanGreen3D* has purchased the Intellectual Property and all of the assets of *Mcor Technologies* on November 29, 2019. *CleanGreen3D* currently offers a *CG-1* 3D printer that uses the same principles (products are made with inkjet printheads, paper, and adhesive) for printing full color, textured, heat resistant, durable, and effective 3D models [16].

FIGURE 11.5 Products made with SDL [14,15]. (Source: *first figure courtesy of [14] and second [15], Euromold 2014).*

11.2.2 Plastic sheet lamination

There are also solutions where a water-based glue is applied on the polymer film, which then the knife cuts into the proper shape. Then, an "antiglue" layer is applied on certain places where there is no cross section of the product, i.e., the glue is neutralized. There are three pens with different tip sizes for antiglue application, so it is possible to apply on the tiniest surfaces. The next layer of film is applied to the previous one and glue is activated by heat during the recoating process. After each layer is glue together, contour is cut with blade. This step is repeated until the final layer of the product. This process was commercialized by *Solido Ltd.*, Israel. Plastic material used in SHL process is thermoplastic material poly(vinyl chloride) (PVC) which has better mechanical properties compared to paper [1–3]. As in other additive manufacturing procedures, the process begins with the lower cross section. When the top layer of the product is finished, the excess material is manually separated from the product (Fig. 11.6). The surface of the product can be postprocessed to avoid the layered structure created by lamination of the layers. The resulting products can be sandblasted, polished, painted, and machined [1–3,17].

Fig. 11.7 shows the products made by PVC foil.

Solido Ltd. was financed by private fund called *Fortissimo Capital* and in 2011 after closing all investment *Solido Ltd.* no longer exist on the market. In February 2011, it was said that they would be taken over by the company *EZ Energy Ltd.*, Israel, but after that there was no more development of 3D printers for production of PVC [18,19].

FIGURE 11.6 The process of separating excess PVC material [3]. *Reprinted from [3], Sheet lamination processes, Copyright (2010), with permission from Springer.*

FIGURE 11.7 Products made of PVC foil [Foto: A. Pilipović, Euromold].

11.2.3 *Sheet lamination of ceramics*

Also with SHL process it can be produced ceramic tapes obtained from green tape casting process or extrusion with thickness from 0.1 to 1 mm. Because of presence of binder, ceramic tapes are flexible and can be cut with laser beam. After lamination, final product is removed from rest of stack and sintered and debound in furnace to achieve full density (approximately 97%), which is actually postprocessing. Ceramics that can be laminated are alumina, silicon nitride, and zirconia. Limitation of this process is binder removal because attachment of two adjacent layers is not as good as internal ones and binder will weaken the interface during burning and evaporation and surface roughness depends on the thickness of the ceramic tapes causing a step effect (R_a is between 2 and 60 μm) [7,20].

11.2.4 *Ultrasonic additive manufacturing*

Metal sheets are laminated with ultrasonic welding which do not require high temperature for bonding. This process is called ultrasonic additive manufacturing (UAM). After production, products require additional postprocessing (e.g., drilling, grinding, and CNC machining for removal of the unbound metal because metal cannot be easily removed by hand). Milling can happen after each layer is added or after the entire process. Advantages of UAM is that with this process different materials can be bond and requires relatively little energy, as the metal sheets are not melted, but instead a combination of ultrasonic frequency and pressure is used to bond the layers together. Materials are bonded by plastic deformation of the metals. Metals that can be used are aluminum, copper, stainless steel, and titanium. Components like thermocouples, fiber optics, or circuits can be laminated between layers of metals, creating a single monolithic part. UAM was commercialized by *Fabrisonic* [21–23].

11.2.5 *Selective lamination composite object manufacturing*

A new development in the SHL process is production of polymer fiber composites which was developed by *EnvisionTEC*. The process is called selective lamination composite object manufacturing (SLCOM). SLCOM is a process that uses woven fiber composites preimpregnated with thermoplastics matrix (something like traditional composite production of prepregs). The roll of prepreg is fed to the machine build platform, then prepreg layers are laminated by means of a heated roller that runs over the entire prepreg and melts the thermoplastic matrix, allowing the layers to be joined together. At the same time inkjet head deposits a waxlike substance in crosshatch area where no lamination is desired. That carbon blade and an ultrasonic emitter cut the fabrics away leaving only the desired product. Whole build area is a table which can rotate in a clockwise or counterclockwise direction, applying the next layer in a different direction very efficiently to build a customized layup sequence [20,24–26]. Postprocessing is not required after lamination.

Unidirectional or multidirectional woven glass, carbon, aramid, poly(oxy benzimidazole) (PBO), and metal fibers like steel, aluminum, and titanium fibers are used for reinforcement and polyamide (PA 6, PA 6.10, PA4.1, PA 11, PA 12), poly(ether etherketone) (PEEK), poly(ether ketoneketone) (PEKK), poly(ether imide) (PEI), poly(phenylene sulfide) (PPS), polypropylene (PP), polyethylene (PE), poly(ethylene terephthalate) (PET), poly(ether sulfone) (PES), and polycarbonate (PC) for the matrix [24].

This technology is used for lightweight structural applications in automotive and aerospace industry, consumer products, sporting goods, and medical devices (Fig. 11.8).

FIGURE 11.8 Polymer composite products made with carbon fiber [24]. (Source: *courtesy of EnvisionTEC GmbH).*

11.2.6 Sheet lamination of textiles

SHL can also be used in the textile industry for production of felt and conductive fabrics. This process was developed by *Disney Research* and *Carnegie Mellon University*. The procedure is similar to the lamination process of the paper or plastic; the layers of fabrics are glued with fusible adhesive and heat, and the contour is cut with a laser in inverted cutting bed to avoid tearing of the fabric. The cutting bed is fixed in place at the top of the printer. Fabric is fed to the bottom face of the bed by rollers mounted to the sides, and held in place by a vacuum during cutting. Cutting is performed by a laser directed through a print head which can move freely in *X* and *Y* below the cutting bed. The print head also carries a downward-facing heated metal disc, which is used to bond layers together. After each layer is bonded, the roller supplies new segment of fabric into place for cutting. The final print is assembled on a bonding platform, which generally remains below the print head, but can raise and lower in *Z* in order to facilitate cutting and bonding operations (Fig. 11.9) [27]. Postprocessing is not required after lamination of the textile.

In textile industry SHL process can be used for production of two different types of fabrics: conductive fabrics and fabrics with integrated sensors (Fig. 11.10).

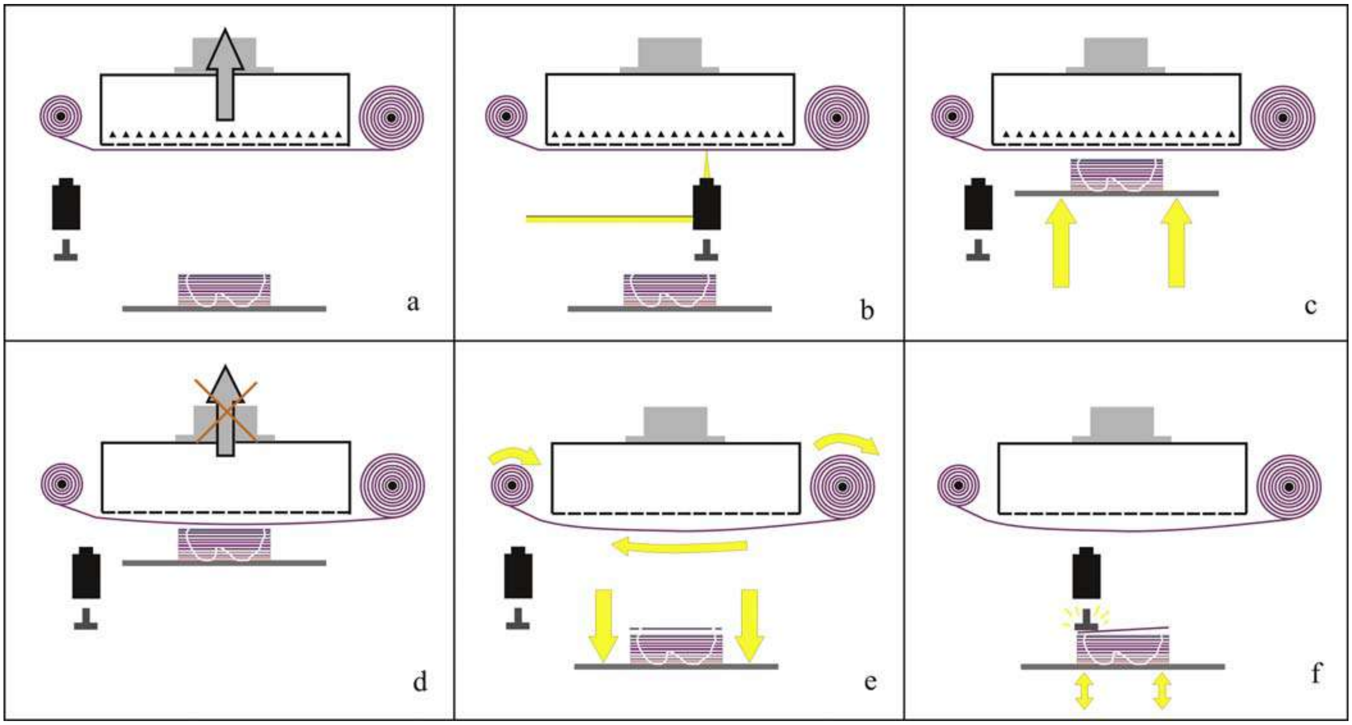

FIGURE 11.9 SHL process for the textiles: (A) vacuum holds the fabric to the cutting table, (B) layer and contour is cut with laser, (C) the bonding platform is raised, (D) vacuum is turn off and freshly cut layer remains on the stack, (E) the bonding platform is lowered and new fabric is supplied with roller, (F) new layer is bonded to the existing layer with the heating disc [27]. *Reprinted from [27], Copyright (2015), with permission from Professor Huaishu Peng.*

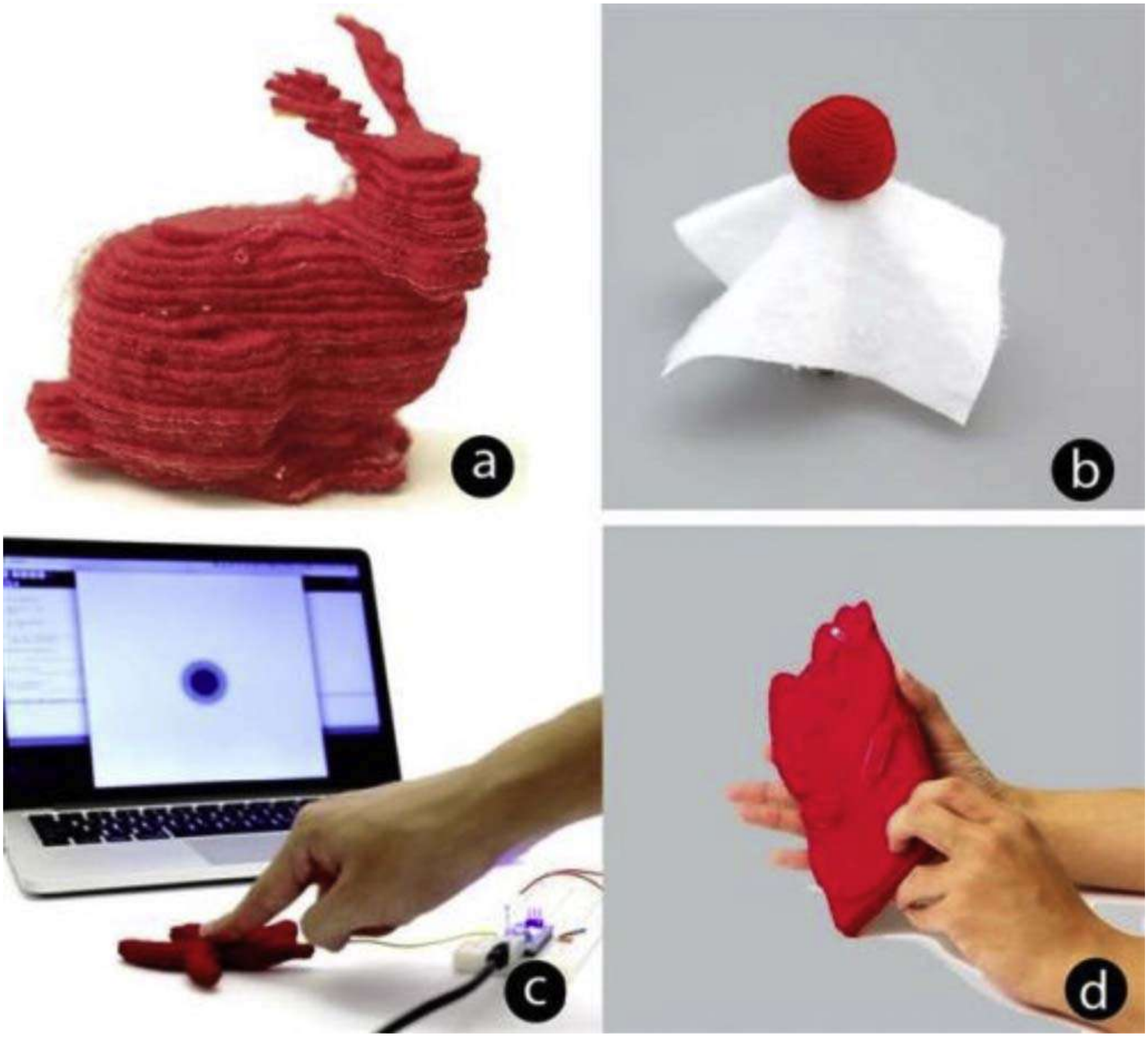

FIGURE 11.10 Production of fabrics with SHL: (A) printed fabric bunny, (B) products with two different fabrics, (C) fabric with integrated touch sensor, (D) printed cellphone case with an embedded conductive fabric coil for wireless power reception [27]. *Reprinted from [27], Copyright (2015), with permission from Professor Huaishu Peng.*

11.3 Advantages and disadvantages of sheet lamination process

The presence of ancillary material around the product has its advantages and disadvantages. First, no external support structure is required. Inside a supporting material, the entire product geometry during manufacturing is protected against deformation due to its own mass. Removing support material after a product has been produced is not an easy task. A careful manual cleaning process is necessary to avoid damaging the sensitive parts and ensuring that only unnecessary material is removed. Furthermore, a hollow structure with a closed surface cannot be treated as a separate part because of the excess material left inside. The difficulty of removing support material applies to all products with narrow channels, restricted inner cavities, indentations, etc. After removing the support structures, this support material cannot be used anymore, so it becomes a waste. The price of such waste is important if materials that are more expensive than paper are used. Furthermore, with its advantages and disadvantages, the SHL process has the following characteristics [2,5]:

- Creates layers that subtract material (e.g., material is cut to create a layer that has the required cross section). All other AM processes form layers by adding material. SHL is potentially the fastest process to produce high volume products;
- The product is formed of alternating layers of materials and adhesives, so the physical properties are inhomogeneous and anisotropic;
- The potential precision of the SHL process is high. Because any thin sheets can be applied in SHL, a good resolution in product design is retained. In fact, the production of thin monodisperse foil material is not difficult and shrinkage during lamination is not a problem as the contours are cut after the shrinkage is complete;
- The process is potentially applicable to many materials, including polymers (only PVC films), papers, composites, metals, and even textiles.

To conclude, the advantages of the SHL process are: high speed, low shrinkage, low warpage, low residual stress, no additional support structure is required, rapid production of large products, machines do not use toxic materials, so no special space is required, in case of using paper low cost of devices and materials compared to other AM processes [1,3,9,10].

Whereas the disadvantages of SHL process are: paper requires the use of protective coatings due to moisture absorption and wear, swelling and uneven thickness of the film makes it difficult to control the accuracy of the dimensions in the *Z*-axis, mechanical and thermal properties are inhomogeneous due to the use of adhesive between layers, removing support material can damage small-scale products and it is time-consuming, inability to manufacture hollow products, small choice of materials in a particular group of materials, large proportion of waste material, anisotropic properties, and strength in Z direction [3,11,12].

11.4 Applications of sheet lamination processes

SHL is not process for the end use parts. SHL is mainly used for prototypes because of its low price of materials, fast production, and the possibility of making products from various types of materials (primarily refers to at least one material within polymers, metals, and ceramics).

With SHL it is not possible to build accurate models such as with PolyJet, stereolithography (SLA), or even selective laser sintering (SLS). It is not possible to print complex geometries, especially hollow structures, but it is cheap process and freeform fabrication processes are making it a good prototyping technique [28].

The main field of SHL application is in education (e.g., how to improve design with additive manufacturing) as it allows you to create products with minimum cost [29]. SHL application is also used for investment casting patterns [14,15], rapid tooling for sand casting (but not for cores with thin walls) [30,31], concept verification, visualization [28], masters for silicone-rubber molds, fit-check, and architecture models (Fig. 11.11) [24,32]. SHL is more popular

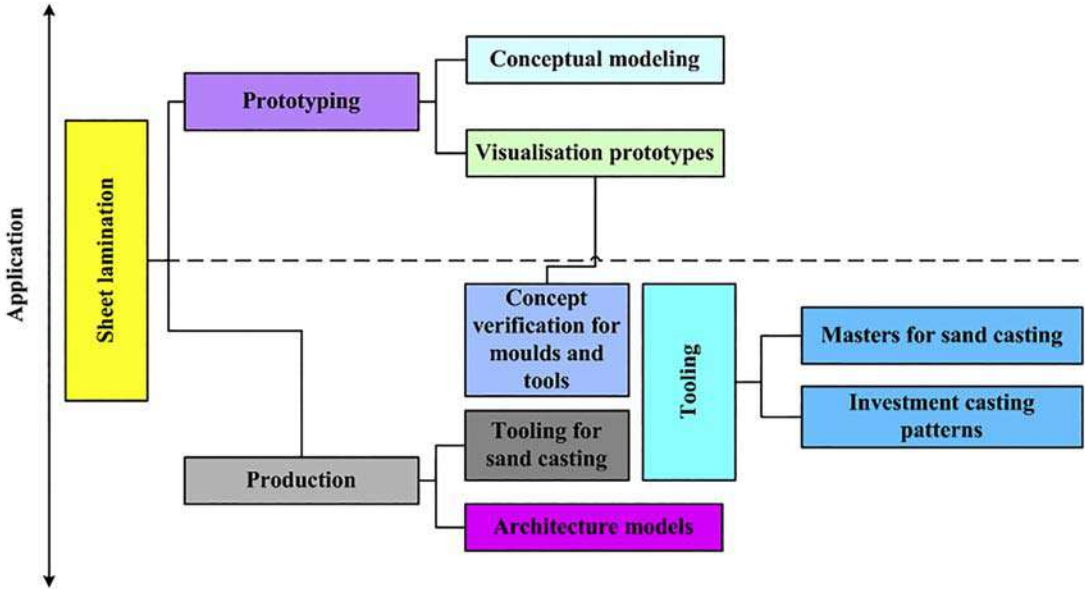

FIGURE 11.11 Application of SHL.

in the production of customized objects than for personal or industrial use. The reason is the fact that at low cost of raw materials, SHL 3D printers are much more expensive than fused deposition modeling (FDM) 3D printers [29].

11.5 Concluding remarks and future insight

The SHL procedure has been in use for 20 years and has had a lot of improvements. From initial application with paper only, SHL 3D printers can also make products from metal, ceramic, thermoplastic, and polymer composites with fibers.

For all its advantages, the SHL process is not as applicable as other processes in additive manufacturing. The reason for this is that although all types of materials can be used, the choice of these materials is very limited especially in polymers. Thus, for example, only PVC and no other thermoplastics material can be used.

Although it is possible to make cheap products with the SHL process, SHL 3D printers are not as cheap as, for example, the printers in FDM process, and it is not possible to obtain complicated geometries with hollow structure as with other AM processes (FDM, DLP, SLA, SLS, 3DP, etc.).

However, the SLCOM process and the application of prepregs with various types of reinforcements/fibers certainly have great potential. Today, composite materials are increasingly used in the military and transport industries (shipbuilding, aviation, automotive, and aerospace), construction, electrical engineering, and medicine, mainly due to their low weight with good mechanical properties (especially high strength and rigidity), resistance to various media, vibration damping, and relatively low production costs.

At the moment, it is not possible to predict how the further development and application of the SHL will go, but certainly the process has its advantages that could bring the SHL process in step with other additive processes.

References

[1] F.W. Liou, Rapid Prototyping and Engineering Applications: A Toolbox for Prototype Development, CRC Press – Taylor & Francis Group, Boca Raton, FL, 2008.

[2] L. Kunwoo, Principles of CAD/CAM/CAE Systems, Addison – Wesley Longman Inc., Reading, MA, 1999, ISBN 0-201-38036-6.

[3] I. Gibson, D.W. Rosen, B. Stucker, Additive Manufacturing Technologies: Rapid Prototyping to Direct Digital Manufacturing, Springer, Boston, MA, 2010.

[4] D.M. Devine (Ed.), Polymer Based Additive Manufacturing, Springer, Cham, 2019.

[5] CustomPartNet, Laminated Object Manufacturing (LOM), https://www.custompartnet.com/wu/laminated-object-manufacturing (Accessed 21 January 2020).

[6] M. Jermann, Laminated Object Manufacturing: LOM, 2003. https://www.makepartsfast.com/laminate-object-manufacturing-lom/ (Accessed 01 February 2020).

[7] M. Brandt (Ed.), Laser Additive Manufacturing Materials, Design, Technologies, and Applications, Woodhead publishing, Duxford, 2017.

[8] A. Gebhardt, Understanding Additive Manufacturing, Carl Hanser Verlag, Munich, 2012.

[9] K.G. Cooper, Rapid Prototyping Technology: Selection and Application, Marcel Dekker Inc., New York, NY, 2001.

[10] G. Gardiner, CompositesWorld, 2017. https://www.compositesworld.com/blog/post/making-composite-parts-from-3d-printed-paper-molds- (Accessed 11 March 2020).

[11] I. Pahole, I. Drstvenšek, M. Ficko, J. Balič, Rapid prototyping processes give new possibilities to numerical copying techniques, J. Mater. Process. Technol. 164–165 (2005) 1416–1422.

[12] T. Lim, J.R. Corney, J.K. Ritchie, J.B.C. Davies, RPBlox – a novel approach towards rapid prototyping, in: A.E.W. Rennie, D.M. Jacobson, C.E. Bocking (Eds.), Proceeding of the Third National Conference on Rapid Prototyping, Tooling and Manufacturing, London, United Kingdom, June 20–21, 2002, Buckinghamshire Chilterns University College, Professional Engineering Publishing Limited, 2002, ISBN 1-86058-374-1, pp. 1–8.

[13] Z.X. Low, Y.T. Chua, B.M. Ray, D. Mattia, I.S. Metcalfe, D.A. Patterson, Perspective on 3D printing of separation membranes and comparison to related unconventional fabrication techniques, J. Membr. Sci. 523 (2017) 596–613.

[14] D. Herzberg, Mcor Makes 3D Printing Improvements that Aren't Paper-Thin, 2015. http://www.dan-herzberg.com/mcor-makes-3d-printing-improvements-that-arent-paper-thin/ (Accessed 20 March 2020).

[15] A. Pilipović, Additive manufacturing processes. Lectures for graduate studies, Faculty of Mechanical Engineering and Naval Architecture, Zagreb, 2017.

[16] Cleangreen3D, https://cleangreen3d.com/ (Accessed 10 July 2020).

[17] D. Godec, Influence of Hybrid Mould on Properties of Injection Moulded Thermoplastic Product, Doctoral Thesis, Faculty of Mechanical Engineering and Naval Architecture Zagreb, 2005.

[18] S. Habib-Valdhorn, 3D Printer Co Solido Lays off Entire Workforce, 2011. https://en.globes.co.il/en/article-1000615567 (Accessed 10 July 2020).

[19] M. Molitch-Hou, What's Going on with Solido? 3D Printing Industry, 2014. https://3dprintingindustry.com/news/whats-going-solido-25400/ (Accessed 10 July 2020).

[20] J. Zhang, Y.G. Jung (Eds.), Additive Manufacturing: Materials, Processes, Quantifications and Applications, Elsevier, Butterworth-Heinemann, Oxford, 2018.

[21] I. Katampe, Innovative applications of polymer materials for 3D printing, in: A.B. Badiru, C.B. Barlow (Eds.), Defense Innovation Handbook, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2019.

[22] O. Diegel, A. Nordin, D. Motte, A Practical Guide to Design for Additive Manufacturing, Springer Nature Singapore Pte Ltd, Singapore, 2020, https://doi.org/10.1007/978-981-13-8281-9.

[23] J.F. Brandon, Fabrisonic – UltraCool Ultrasonic Additive Manufacturing, 2015. https://www.solidsmack.com/fabrication/fabrisonic-ultracool-ultrasonic-additive-fabrication/ (Accessed 02 April 2020).

[24] EnvisionTEC, https://envisiontec.com/3d-printers/slcom-1/ (Accessed 03 April 2020).

[25] M. Molitch-Hou, Envision TEC Blows Up Rapid with Mega Composite 3D Printer and More, 2016. https://www.engineering.com/BIM/ArticleID/12210/EnvisionTEC-Blows-Up-RAPID-with-Mega-Composite-3D-Printer-and-More.aspx (Accessed 05 April 2020).

[26] G. Gardiner, Three New 3D Printnig Technologies for Composites, CompositesWorld, 2016. https://www.compositesworld.com/blog/post/three-new-3d-printing-technologies-for-composites (Accessed 05 April 2020).

[27] H. Peng, J. Mankoff, S.E. Hudson, J. McCann, A Layered Fabric 3D Printer for Soft Interactive Objects, Design and 3D Object Fabrication CHI 2015, Crossings, Seoul, 2015, pp. 1789–1798, https://doi.org/10.1145/2702123.2702327.

[28] Sculpteo, LOM (Laminated Object Manufacturing): 3D Printing with Layers of Paper, 2009–2020, https://www.sculpteo.com/en/glossary/lom-definition/ (Accessed 10 July 2020).

[29] 3D Print Expo, Laminated Object Manufacturing, 2017. https://3d-expo.ru/en/article/izgotovlenie-obektov-metodom-laminirovaniya-lom-78841 (Accessed 10 July 2020).

[30] B. Mueller, D. Kochan, Laminated object manufacturing for rapid tooling and patternmaking in foundry industry, Comput. Ind. 39 (1999) 47–53.

[31] W. Wang, J.G. Conley, H.W. Stoll, Rapid tooling for sand casting using laminated object manufacturing process, Rapid Prototyp. J. 5 (3) (1999) 134–140.

[32] S. Jeong, J. Sim, H. Kim, D. Shin, D. Hong, Application of LOM freeform architecture, J. Korean Soc. Precision Eng. 34 (12) (2017) 903–909.

C H A P T E R

12

Direct energy deposition

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12.1 Introduction

Additive manufacturing (AM) uses an advanced technology which utilizes 3D computer-aided design (CAD) model for fabricating three-dimensional (3D) parts directly [1]. In this process, the targeted part is manufactured by deposition method in a layer-by-layer fashion [2]. AM techniques are further divided into seven different types, viz. binder jetting, direct energy deposition (DED), material extrusion, material jetting, power bed fusion (PBF), sheet lamination, and vat photopolymerization [3]. In this section we will focus on DED which is a subpart of AM.

In DED method, thermal energy is employed to fuse and melt the materials which are being deposited simultaneously [1,4–6]. The thermal source can be either of laser beam (LB), electron beam (EB), or arc plasma energy sources [7]. Depending on usage of the source, DED is categorized into different types: laser engineered net shaping (LENS), laser solid forming (LSF), direct light fabrication (DLF), direct metal deposition (DMD), electron beam AM (EBAM), and Wire and Arc AM (WAAM) [8]. The working principle in all categories remains the same. In the process of DED an inert atmosphere is maintained, and then the feedstock material (wire or powder) is fed coaxially to the thermal source. It gets melted due to heat from the thermal source and the layer is built on the targeted local site. Then, from the thermal energy source the beam or arc is focused upon a small region of the targeted substrate material [8–10]. The whole process occurs in a cycle, in which the high power-density nozzle with a concentric laser or electron beam is focused onto a part of surface to create melted pool of the surface material. Then, the melted material is delivered in the form of powder or wire through a coaxial nozzle (for laser) or through a metal wire with a side delivery (for electron beam). Then this nozzle moves at a constant speed and follows a determined path assisted by data fed by CAD. The melted material solidifies as soon as the nozzle moves away from the melted pool of the surface material. There are further successive layers formed in the same cycle forming layer by layer on top of each new layer until it is completed. The resolution of DED process is highly dependent on the type of energy source and the heat output during the manufacturing process. The resolution of DED has the following trend [11,12]:

$$\text{Laser} > \text{Electron beam} > \text{Arc.}$$

Also, the fabrication speed during the manufacturing process is of utmost important which decides the intricacies required for the targeted parts. The laser absorbed (W_a) during the manufacturing process by the material can be simplified using Eq. (12.1) [11].

$$W_a = AP_L t_i \tag{12.1}$$

in which:

A = Heat absorptivity of laser beam on surface of the substrate metal,
P_L= Power of the laser beam,
t_i = Interaction time of the laser beam with the surface of the work piece.

Polymers for 3D Printing
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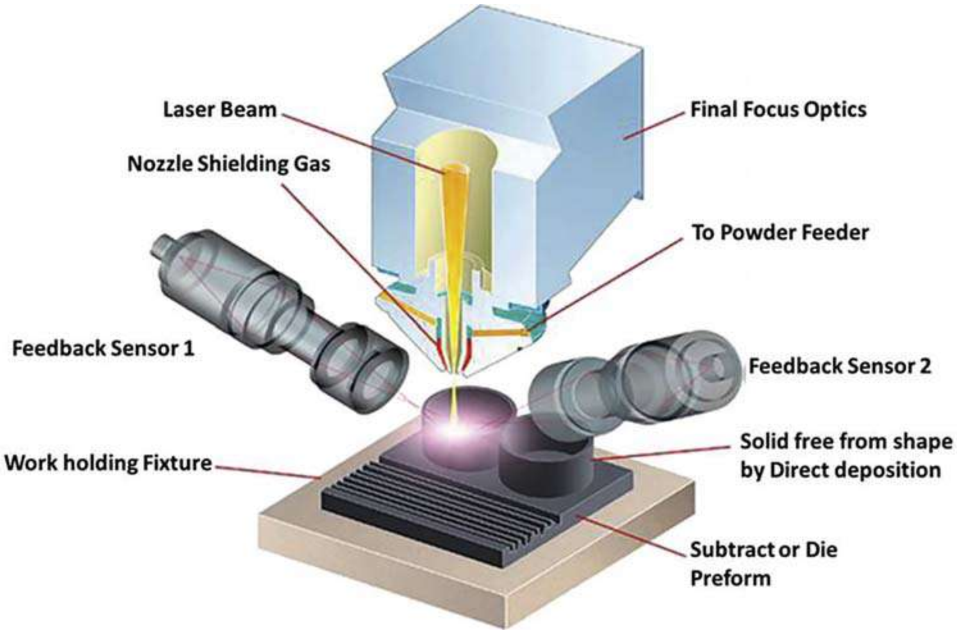

FIGURE 12.1 Schematic arrangement of DED technology. *This figure is reprinted with permission from Ref. [12], Copyright (2016) Elsevier.*

which can be further expressed with the diameter of the laser beam (d) and the laser scanning speed (v) (Eq. 12.2).

$$t_i = \frac{d}{v} \tag{12.2}$$

Fig. 12.1 shows the arrangement of the laser beam nozzle along with two feedback sensors for DED.

12.2 Polymer DED technology

Polymer DED technology is the extended techniques arising from DED method. In which, a part of 3D metal that has to be printed is fused with plastic polymer using the direct laser irradiation. It employs usage of bonding technique on the metal surface which has no patterns, with another metal surface which is patterned and printed by microlaser. Printing by the microlaser ensures proper joining of the metal with each other. Also, there were different set of experiments that were conducted by placing a metal 3D printing material at the bottom, placing a polymer material at the top, and irradiating a laser on the surface of the metal 3D printing material. The studies concluded that when using laser micropatterned metal surface, the adhesion of the polymer was far better than the ones with smoother surfaces. The better bonding can be compensated due to better anchoring of polymer molecules to the metal surface. This resulted into better polymer adhesion to heterogeneous materials.

A modified version of polymer DED technology is being employed by a company named AREVO; it uses the polymer extrusion feeding in the form of carbon fiber along with the laser energy source for fabrication of lightweight composite print parts for various applications. The method starts with the heating and melting of the thermoplastic material by using any of the thermal sources like electron beam, laser, or plasma arc. Later, this melted polymer material is then pressed between the rollers for compact layering of the object [13] (Fig. 12.2).

By the polymer DED process developed by AREVO company, it was proven that a carbon fiber based either in the form of wire or filament can be impregnated by thermoplastic polymer matrix without the need of controlled environment. Later it was molded into permanent shapes. This results in stronger structures than before. The composites were light in weight, stronger, and also stiffer.

They exhibited good tensile strength and chemical and heat resistance. Using this polymer DED technique, AREVO Company was able to print objects up to 1 cubic meter. Furthermore, few other modifications were also made to laser polymer DED method by AREVO, which included the laser thermal source to melt the polymer filament simultaneously, i.e., melting the previously deposited material to create an in situ consolidated liquid−liquid interface. It helps in applying the force of compression to reduce the number of voids in the composite and avoids layers within the composite to maintain the homogeneity. The schematic diagram (Fig. 12.3) explains the arrangement of polymer DED technology [13,14].

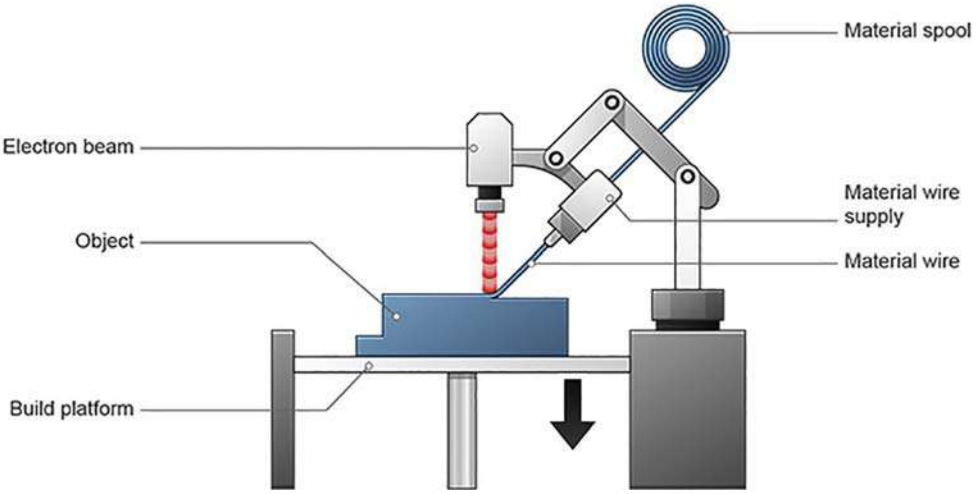

FIGURE 12.2 Schematic arrangement of DED additive manufacturing process using an electron beam. *This figure is reprinted with permission from Ref. [13], Copyright (2019).*

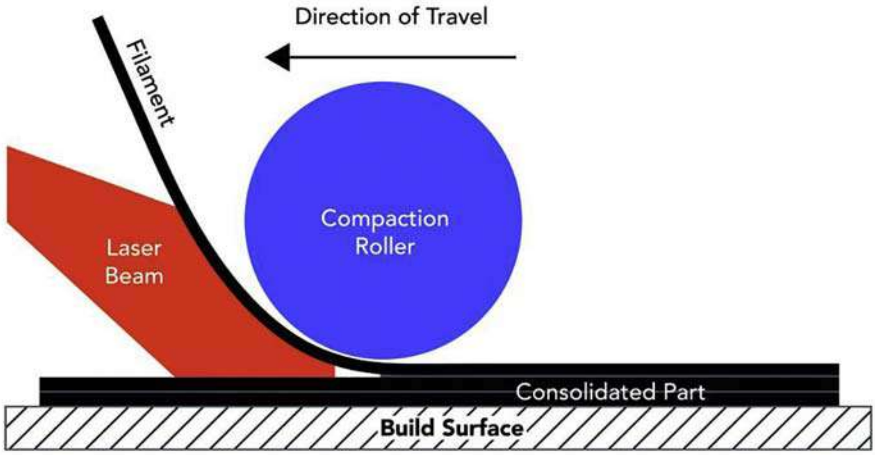

FIGURE 12.3 Schematic arrangement of polymer DED technology at AREVO. *This figure is reprinted with permission from Ref. [14], Copyright (2020) AREVO.*

12.3 Advantages and disadvantages of polymer DED technology

Polymer DED technology has more advantages over traditional DED methods which includes prevention of deflection of electrons that interact with air molecules. Compared to the metal-based DED method polymer DED has high-throughput ratio and it gives an upper hand to process multimaterials together, with sophistication of manufacturing large parts. With the use of completely inert chamber it can accommodate use of reactive metals for making polymer composites. It allows for in situ consolidation of the polymer matrix which reduces the cycle time and production steps. Due to presence of significant quantity of inert gas available, the metal that is being deposited along with the polymer is free from contamination. Also, this process allows masking the shielding gas which is being used for the manufacturing process. The systematic use of automated robotic 3D printer gives upper hand over manual errors and curing steps completely, which helps in producing parts and products almost instantly. The whole manufacturing process can be customized as per the demand with process repeatability. The polymer DED technology helps to make polymer–metal composites which are light-weighted, low void content, unlimited part size with high strength-to-weight ratios which often serves as replacements of several metal parts and assemblies. These features enable printing complex geometrical parts with ease and without support structures. Polymer DED process helps in reducing material costs and increases mechanical performance of the material. Moreover, it eases the pain of making complex single parts into a single simple part without any external need for joints. The labor costs as well as production time can be reduced drastically by using polymer DED technology. Also, one of the biggest advantages is to engineer items without using any other extra tools, for example, making a one frame single molded electric bike [13—16].

The major disadvantage of metal-based polymer DED technology is that it requires use of controlled environment chamber which needs large amount of inert gas to be supplied continuously. Sometimes, it becomes difficult to reach the anticipated levels of inert gas for the manufacturing process within required time limit [12—14]. Along with that it also requires huge capital cost to start and maintain the manufacturing processes. Another disadvantage of DED polymer technology is that it builds low resolution parts which undergo another round of processing to get the finished look that adds on more investment of time and cost. It also lacks support structures during the build process which restricts some essential features like overhangs [17].

12.4 Applications of polymer DED technology

The ability to repair and produce the damaged parts of the existing instrument or equipment of the metal DED technology when blended with polymer DED it works wonder. Due to which it can have myriad of applications in various sectors including aerospace, automotive, sports, and construction industries. Light-weighed components in aerospace, wheels, e-vehicles including electric bikes and scooters, frames of automobile, drones, sporting goods like tennis racquet, and construction industries can be designed and developed using polymer DED technology [14,16,18].

Fig. 12.4 shows the graph of other metal AM technologies with different processes in which powder and wire DED is considered to be better than others in terms of cost and product manufacturing. Furthermore, Fig. 12.5 gives

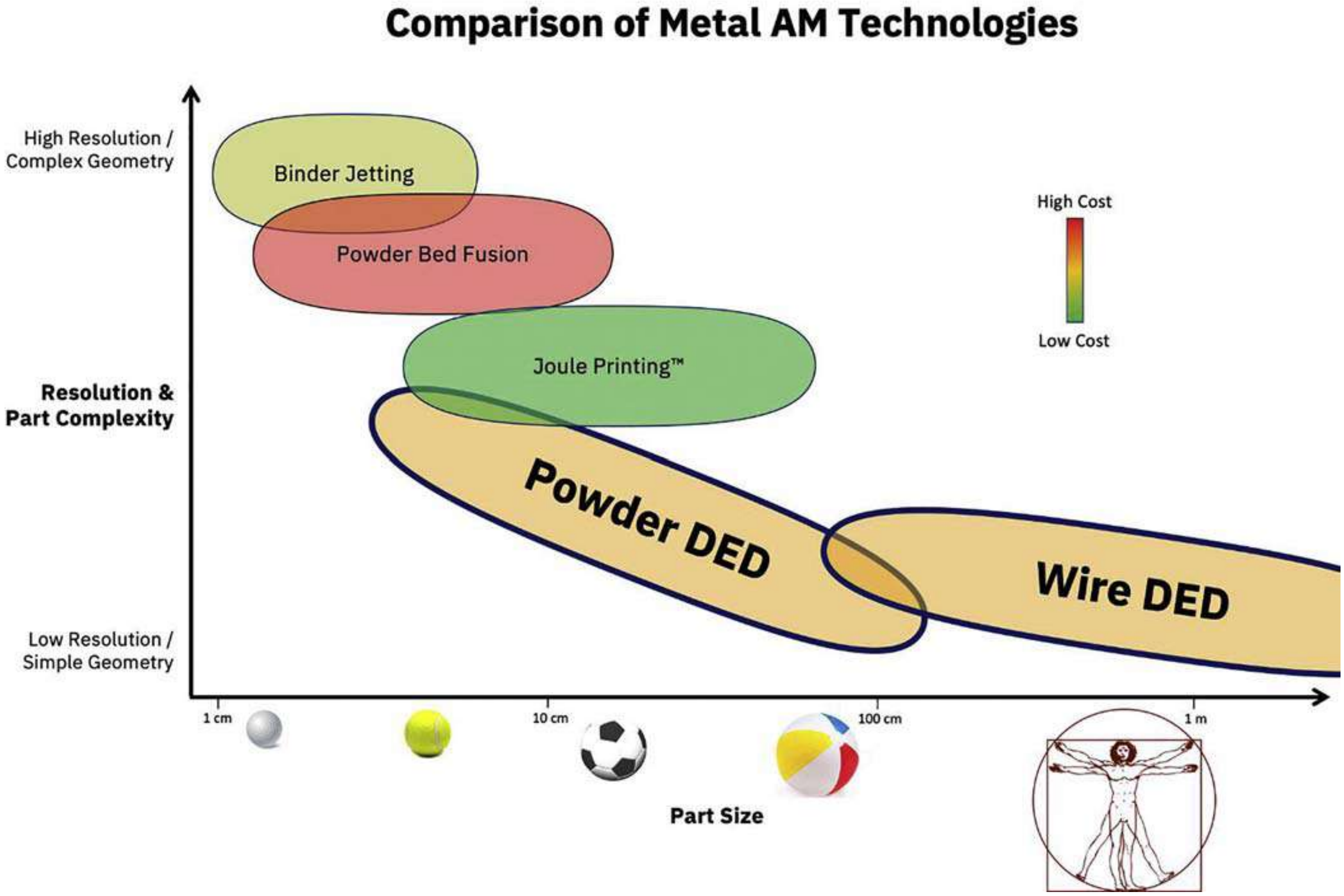

FIGURE 12.4 Comparison of metal AM technologies. *This figure is reprinted with permission from Ref. [19], Copyright (2019) Digital Alloys Inc.*

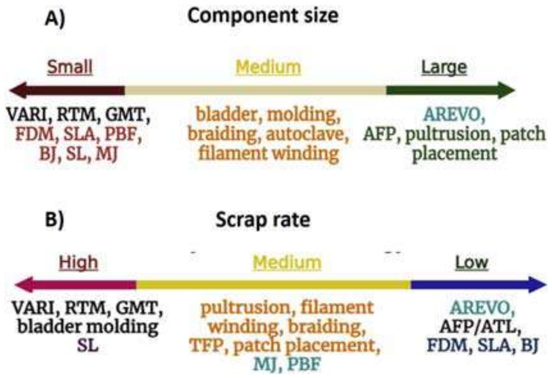

FIGURE 12.5 (A) Process comparison regarding component size (*FDM*, Fused Deposition Modeling; *SLA*, Stereolithography; *PBF*, Powder Bed Fusion; *BJ*, Binder Jetting; *SL*, Sheet Lamination; *MJ*, Material Jetting). (B) Process comparison regarding scrap rate. *This figure is reprinted with permission from Ref. [16], Copyright (2019) AREVO.*

comparison of the component size and the scrap rate obtained due to various other technologies when compared to polymer DED. This proves it has better applicability over wide range of sectors.

12.5 Concluding remarks and future insight

It is predicted that in the near future there is an immense scope for development of polymer DED technology considering the current trends. It has given a multiway usage channel for different industries with an ease in manufacturing according to the customers' demands. Though it has low scrap production rate, it lacks high resolution. It has made easier for designers to create complex composite designs within their reach based on various comprehensive data and structural analysis. Further research would be needed to overcome the bonding issues with dissimilar materials without the need of external laser patterned printed material. The extensive finishing of the products manufactured by polymer DED technology can be an area of interest for researchers. Nevertheless, there is yet more to be discovered as additional features in repairing applications [13,16,19].

References

[1] A. van Wijk, I. van Wijk, 3D Printing with Biomaterials: Towards a Sustainable and Circular Economy, IOS Press, 2015, pp. 11–12, https://doi.org/10.3233/978-1-61499-486-2-i.

[2] J. Scott, N. Gupta, C. Weber, S. Newsome, T. Wohlers, T. Caffrey, Additive Manufacturing: Status and Opportunities, Science and Technology Policy Institute, Washington, DC, 2012, pp. 1–29.

[3] Technologies, A.C.F.o. A.M. and A.C.F.o.A.M.T.S.F.o. Terminology, Standard Terminology for Additive Manufacturing Technologies, ASTM International, 2012.

[4] H.-K. Lee, Effects of the cladding parameters on the deposition efficiency in pulsed Nd:YAG laser cladding, J. Mater. Process. Technol. 202 (2008) 321–327.

[5] Q. Zeng, Z. Xu, Y. Tian, Y. Qin, Progress of the Modelling of a Direct Energy Deposition Process in Additive Manufacturing, 2016. https://pure.strath.ac.uk/ws/portalfiles/portal/53263709/Zeng_etal_ICMR2016_progress_modelling_direct_energy_deposition_process_additive_manufacturing.pdf (Accessed 10 February 2021).

[6] D.-S. Shim, G.-Y. Baek, J.-S. Seo, G.-Y. Shin, K.-P. Kim, K.-Y. Lee, Effect of layer thickness setting on deposition characteristics in direct energy deposition (DED) process, Opt Laser. Technol. 86 (2016) 69–78, https://doi.org/10.1016/j.optlastec.2016.07.001. ISSN 0030-3992.

[7] I. Gibson, D. Rosen, B. Stucker, Directed energy deposition processes, in: Additive Manufacturing Technologies: 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing, vol. 68, Springer New York, New York, NY, 2015, p. 245.

[8] T.D. Ngo, A. Kashani, G. Imbalzano, K.T.Q. Nguyen, D. Hui, Additive manufacturing (3D printing): a review of materials, methods, applications and challenges, Compos. Part B 143 (2018) 172–196.

[9] R. Liu, Z. Wang, T.E. Sparks, F.W. Liou, J.W. Newkirk, 13—Aerospace Applications of Laser Additive Manufacturing A2—Brandt, Milan, Laser Additive Manufacturing, Woodhead Publishing, 2017, pp. 351–371.

[10] K.V. Wong, A. Hernandez, A review of additive manufacturing, ISRN Mech. Eng. 208760 (2012) 10.

[11] M. Labudovic, D. Hu, R. Kovacevic, A three-dimensional model for direct lasermetal powder deposition and rapid prototyping, J. Mater. Sci. 38 (2003) 35–49.

[12] B. Dutta, F.H. Froes, Chapter 3, Additive Manufacturing Technology, Additive Manufacturing of Titanium Alloys State of the Art, Challenges and Opportunities, 2016, pp. 25–40.

[13] V. Carlota, The complete guide to directed energy deposition (DED), 3Dnatives, 2019. https://www.3dnatives.com/en/directed-energy-deposition-ded-3d-printing-guide-100920194/ (Accessed 10 September 2019).

[14] H.B. Martin, Arevo's new design-print-go additive manufacturing system speeds parts-building, 2020. https://www.thefabricator.com/additivereport/article/additive/arevos-new-design-print-go-additive-manufacturing-system-speeds-parts-building (Accessed 4 February 2020).

[15] S. Nathan, In the frame: the 3D printed bike, The Engineer, 2020. https://www.theengineer.co.uk/frame-3d-printed-bike/ (Accessed 27 January 2020).

[16] L. Langnau, What Is Polymer Direct Energy Deposition (DED) for 3D Printing and How Can it Benefit You, Design World, 2019. https://www.designworldonline.com/what-is-polymer-directed-energy-deposition-ded-for-3d-printing-and-how-can-it-benefit-you/ (Accessed 26 July 2019).

[17] Directed Energy Deposition (DED), What is Directed Energy Deposition?, 2021. https://engineeringproductdesign.com/knowledge-base/direct-energy-deposition/ (Accessed 10 February 2022).

[18] AREVO, Applications, 2021, https://www.arevo.com/applications/lightweighting?lang=en (Accessed 10 February 2022).

[19] Y. Bandari, R. Wilson, M. Pieger, M. Lang, J. O'Hara, N. Mayer, Directed Energy Deposition (DED), Digital Alloys' Guide to Metal Additive Manufacturing — Part 9, Article Blog, Digital Alloys, 2019. https://www.digitalalloys.com/blog/directed-energy-deposition/ (Accessed 10 June 2019).

PART III

Polymers used in 3D printing—properties and attributes

CHAPTER

13

Photopolymers for 3D printing

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13.1 Introduction

3D printing or additive manufacturing (AM) is a process in which objects are subsequently fabricated in a layer-by-layer fashion giving rise to materials having high precision [1]. The main advantage is not only its high accuracy, but generation of less waste products compared to other conventional processing techniques. Photopolymers have been greatly explored in the field of AM for the fast and effective polymerization of solvent-free liquid resins. To be simple, photopolymers being used for 3D printing and 4D printing are light-sensitive polymer materials that can change their physicochemical properties when exposed to light. The commonly employed polymer bases are polyvinyl cinnamate, polyamide (PA), polyisoprene, polyimides, epoxies, acrylics, etc. Usually a photopolymer consists of monomers, oligomers, and photoinitiators that undergo curing in presence of light (ultraviolet, visible), whereby the liquid resins get hardened and form a solid polymeric material (Fig. 13.1) [2]. Generally a photoinitiator or photoinitiator system (having relatively high absorption coefficients) is required to convert photolytic energy into the reactive species (radical or cation) which drives the chain growth via radical or cationic mechanism [3]. Photopolymerization-based 3D printing techniques like stereolithography, digital light processing (DLP), continuous liquid interface production (CLIP), two-photon polymerization, and lithography-based 4D printing make use of light-sensitive resins which are cured layer by layer using a laser or digital light source. Parameters like the wavelength and the intensity of the light source play a very crucial role in formulating the ink, particularly the photoinitiators [4]. Hence for an effective polymerization, all these variables including printing parameters need to be tailored. Resin is a general name used to describe different kinds of polymers, polymer pioneer

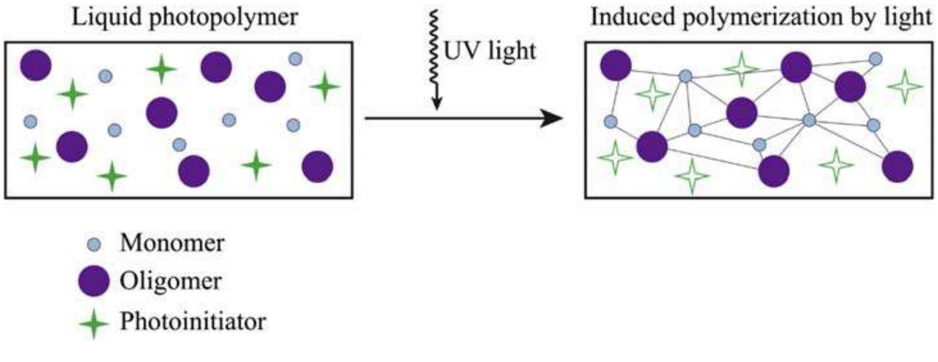

FIGURE 13.1 Schematic representation of photopolymerization process [2].

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[a] These authors have equally contributed.

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constituent, and/or concoction or composition containing several components or chemically responsive elements [5]. For biomedical applications, it is highly desired that the resin be biocompatible having good mechanical properties. Lim et al. employed biocompatible monomers polyethylene glycol diacrylate (PEGDA) and vinyl pyrrolidone (VP) for 3D printing microneedles. The drug acetyl-hexapeptide 3 was loaded into the resin. The drug retained its stability throughout, and the final polymer also had minimal cytotoxicity to human dermal fibroblast cells [6]. This chapter gives an insight into the various photopolymers and their characteristics. The processing techniques along with applications have also been described.

13.2 Processing techniques of photopolymers

3D printing technology was developed few years ago to fabricate different types of products, primarily for prototyping. 3D printing can include a cluster of systems, which could make use of methods such as photopolymerization, powder solidification, sheet lamination, extrusion, direct energy deposition, etc. It aids the conversion of simulated, computer-generated representations into 3D perceptible items by means of layer-by-layer (LbL) deposition [7–9]. ASTM F42 classifies AM processes into seven major categories, namely, photopolymerization, material extrusion, sheet lamination, material jetting, direct energy deposition, binder jetting, and powder bed fusion [10], and their prominent details are shown in Table 13.1 [11].

Stereolithography (SLA), a.k.a. vat photopolymerization, is a technique employed for creating 3D structures by means of light-emitting systems (DLP or laser) which irradiates and cures photo resins (mostly thermosetting plastics) in a layer by layer fashion (Fig. 13.2). SLA is capable of delivering unique properties and ensuring a fine layer quality with a limited stair step impact [13,14]. The rapid development of AM via stereolithography is indeed remarkable and demonstrates a significant technical advance with a huge potential for diverse applications [15]. SLA can be employed with the help of various resins such as standard (rigid, opaque), flexible, castable, high-temperature, and transparent types. Injection molds and mold patterns (i.e., direct and indirect rapid tooling) are fabricated utilizing high-temperature and castable SLA resins, respectively [16]. The peculiar photo-induced polymerization exclusively along the irradiated zones of SLA 3D printing achieves the development of high-resolution assemblies relative to other AM strategies including selective fused deposition design, laser sintering, and laminated structure production [12,17].

TABLE 13.1 Techniques for photopolymer AM.

No.	Technique	Starting material	Example polymers	Approach	Resolution (μm)
1	Stereolithography (SLA)	Liquid resins	Epoxy resins/acrylate based	Laser scanning polymerization	<10
2	Micro-SLA	Liquid resins	Epoxy- or acrylate-based resins	Super-resolution laser scanning polymerization combined with inhibition	0.1–0.5
3	Digital light processing (DLP)	Liquid resins	Resins reinforced with diverse particles	2D projection, selective surface polymerization	≈10
4	Two-photon polymerization	Liquid resins	Epoxy- or acrylate-based resins	Polymerization requiring two photons to cleave photoinitiator, reducing polymerization cross section	≈0.01
5	Volumetric printing	High viscosity liquid or thermally gelled resins	Methacrylate, gelatin, acrylate resins	Tomographic printing	≈300
6	Inkjet printing	Liquid resins, shear-thinning	Liquid gels, pastes, hydrogels based on PLA	UV assisted or thermal curing; extrusion	5–200

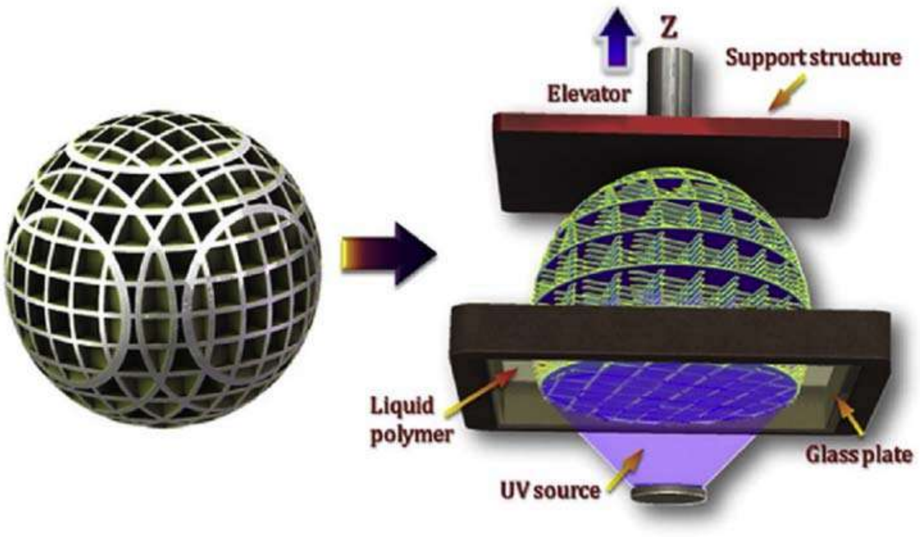


FIGURE 13.2 Design of an SLA 3D printer [12].

In the case of resins designed for AM, the practice of adopting several radical photoinitiators is quite prevalent, and the efficacy of this approach will be primarily dependent on the wavelength breadth of the light source. The recent advancement of the SLA 3D printing system, like that of the continuous liquid interface production (CLIP), solves some of the previously recorded shortcomings by hitting new milestones in the efficiency of the printing process without losing its precision [18]. The CLIP approach benefits free radical polymerization and its oxygen inhibition in photopolymerizing UV-curable resins that preserve a coating of liquid at the bottom of the resin reservoir during oxygen-permeable membrane polymerization [12]. Photoinitiators translate light energy into chemical energy because the liquid resin interacts with a UV light source, generally a torch, laser, or projector. Oligomers and monomers then mix, toughen, and create connections that construct the polymer structure [19].

Like their thiol-ene counterpart, AM based on vat photopolymerization method was used to start the photochemical path for the thiol-yne addition reaction. Within the formulation of photo resins, scientists effectively formulated an aliphatic polycarbonate oligomer with a pendant alkyne functional group as a hydrolytically compostable 'yne' portion, which was in effect implemented in printing structures with high resolution (50 μm layer thickness) via DLP 3D printing [20]. The efficiency of the radical photoinitiator used would rely on the source of light employed.

DLP is an optical AM technique that utilizes vat photopolymerization for the creation of diverse intricate forms with high versatility in nature. DLP uses light with high resolution that can efficiently polymerize a thin film of a photocurable resin in the X, Y, and Z directions, achieving an accuracy of tens of micrometers. The limited utilization of raw materials together with the attainment of products with a better resolution by eco-engineering precepts are also benefits of the DLP process [8,21,22]. Selective laser (SL) makes use of photopolymer liquid as a base for the formulation for product fabrication. The photopolymer is toughened and cured to create a coating by screening the laser beam. The process persists layer-wise till the whole product is completed [23]. Ultraviolet curable nanoimprint lithography (UV-NIL) entails impressing with UV exposure on a sheet of liquid photopolymer resist and curing, which allows the resist to stiffen owing to the polymer cross-linking as an alternative to controlling the change in phase through resist temperature. This is different from the thermal NIL process, but the remaining mechanism is analogous to the thermal NIL process [24].

Liquid resins–based AM technologies such as stereolithography (SLA) and DLP show higher resolution and accuracy than other printing technologies together with good Z-axis strength when compared with the other commercially available 3D printing technologies [25]. The bases for both these techniques are the selected rapid conversion of oligomers to solid photopolymers when irradiated by UV light or laser [3,26]. The high resolution of SLA and DLP technique in the $X-Y$ plane is ascertained by the very small optical spot sizes from the laser or projector [27]. By analyzing the curing depth, *Z*-axis resolution can be assessed, and recently it was found that by using micro-SLA and UV-laser, resolution up to even 10 nm can be achieved [28]. Also, it was recently described that by using the two-photon initiation approach, fine *Z*-axis resolution up to 100 nm can be determined [29]. During printing, by closely attaching each new layer to the preceding layer in the liquid resin, a smooth surface and good *Z*-axis strength can be attained as less force will be applied to the printed object [30]. However, the current printing techniques are having the limitation of single material printing thereby affecting the degree of material variations, thereby limiting the intended functions of the resulting final objects. Hence, to enhance and broaden the applications of SLA and DLP technologies in the manufacturing and healthcare industries, the progress of the functional resins is significantly preferred. Printable materials are mostly comprised of monomers, oligomers, and photoinitiator systems in photochemistry based AM systems. Initiating species like radicals are produced by a photochemical reaction under light irradiation which is controlled or later drawn by CAD at room temperature, which is then used with monomer units in the 3D printing process [31]. Thus, in 3D printing polymer-based objects, light-induced polymerization is well suited and studied. For biological applications owing to the different reaction temperatures and the ease of sustaining sterile conditions, specially formulated reactive liquids can be rapidly altered into solids at ambient temperature, and the process is therefore particularly interesting. With holographic materials formed entirely of photopolymers, large index modulation is difficult to attain [32]. So, to enrich large index contrast in such materials, distinctly separate polymerization of different low and high index monomers is required.

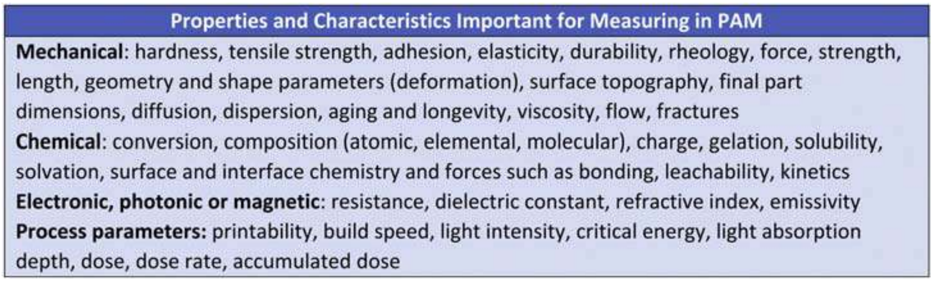
13.3 Characteristics and properties of photopolymers

Photopolymers, also known as UV resins employed in stereolithography are usually acrylic and epoxy resins [33]. These are either thermoplastics, that melt at elevated temperatures, or thermosets, which once cured by heat, do not undergo melting or reshaping. They are well-suited for various AM procedures. A resin is cured with light in all of these methods, so a complete component or prototype is formed layer by layer before completion [11,19,34].

The recoating depths or thickness of coated layers prior to curing is an essential parameter for all kinds of photopolymers used in AM. Recoating limitations vary based on both the building process and the resin. The resin's viscosity and wettability on the solidified component are also vital in such cases. Therefore, the acrylates with a higher molecular weight typically used for AM frequently have to be thinned with a smaller but still multifunctional component [18,35]. Among the most widely employed types of monomeric units for photo-based AM include epoxides. One explanation is that during photo-cross-linking, epoxides experience pointedly reduced shrinkage (volumetrically 2%–3%) when compared to acrylates. Another factor might be the relatively strong mechanical properties of the resulting polymers. 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ECC), diglycidyl ether derivatives of bisphenol A (DGEBA), and epoxides of aliphatic alcohols like trimethyloyl propane are perhaps the most widely employed epoxide monomers for SLA [36].

Even during the initial periods of using SLA, the benefits of using resins composed of various forms of monomers with varying reaction rates were already known. Since the photopolymerization of epoxide monomeric units is much slower than that of acrylate monomers, they are seldom utilized individually in AM photo resins. The benefit of employing vinyl ethers in conjunction with epoxides is that throughout the AM design procedure the former will quickly polymerize and harden enough, while the second will reduce shrinkage during the post-cure process. Acrylates and epoxides encounter multiple polymerization phases and do not markedly interfere with each other. It is noteworthy that the resulting polymer is thus an interpenetrating network (IPN), vinyl ether/epoxy mixtures, and acrylate/methacrylate, for example, and not a copolymer. A benefit of these devices is a substantial drop in oxygen inhibition sensitivity [18,37]. A photo resin solution composed of both acrylate and methacrylate has been stated to be superior because methacrylates recover on their own too slowly and because the pure acrylate system contributes to alterations in the printed item. Owing to the mechanical strength these functional groups offer, resins based on urethane acrylates and DGEBA (bisphenol A diglycidyl ether) are employed widely [36,38].

Additives other than monomers and initiators are also included in photo resins for AM processes, among which low radical inhibitor concentrations are required to avoid premature gelation of acrylates [18]. In several patents, substituted anthracenes and pyrene are identified to function as both light absorbers and sensitizers for stereolithography. The main purpose of light absorbers is to reduce D_p (penetration depth) more accurately, especially when photosensitizers allow curing of higher wavelength light sources or lowering of E_c (critical exposure) at a specific wavelength. Simply reducing D_p facilitates finer surfaces and therefore improved z-resolution, and enables the formation of cut structures that are not feasible otherwise [36]. Experimental findings by Wang and coworkers showed



Properties and Characteristics Important for Measuring in PAM

Mechanical: hardness, tensile strength, adhesion, elasticity, durability, rheology, force, strength, length, geometry and shape parameters (deformation), surface topography, final part dimensions, diffusion, dispersion, aging and longevity, viscosity, flow, fractures

Chemical: conversion, composition (atomic, elemental, molecular), charge, gelation, solubility, solvation, surface and interface chemistry and forces such as bonding, leachability, kinetics

Electronic, photonic or magnetic: resistance, dielectric constant, refractive index, emissivity

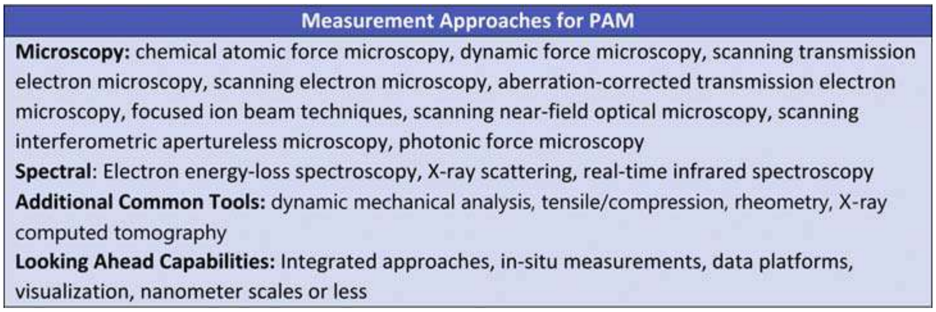
Process parameters: printability, build speed, light intensity, critical energy, light absorption depth, dose, dose rate, accumulated dose

FIGURE 13.3 Relevant properties and characteristics for the assessment of photopolymer additive manufacturing (PAM) [11].

that tension stress amplified faster for tensile experiments at a higher strain rate. The preload strain rate for relaxation testing has also been found to affect relaxation stress [39].

A detailed list of substantial properties and characteristics for evaluating photopolymer AM and their measurement techniques are provided in Figs. 13.3 and 13.4, respectively [11].

Monzon et al. reported the fabrication of castable resins by DLP [40]. In the study, the photopolymer blend consisted of acrylate/glycol diacrylate monomers with phosphine oxide-based photoinitiator. UV having a wavelength of 315–400 nm was employed for curing. The resin required longer curing times for about 40 min. The castable blend remained nonisotropic due to the nonsoluble pigments that created UV barrier. It was thus concluded that post-curing could remove anisotropy in those resins where the pigment does not obstruct the passage of UV light through the liquid resin. The field of dentistry has greatly benefitted from 3D printing technology [41]. Resin-based dental restoratives were introduced in 1960 and have been exploited as dental restorative materials. Initially chemically cured materials were used which was later on replaced by UV-cured materials. Thereafter visible light curing materials comprising of photoinitiator camphorquinone (CQ) followed. Dental resins were prepared by the photopolymerization of bisphenol A glycol dimethacrylate (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA), urethane dimethacrylate (UDMA), and ethoxylated bisphenol A glycol dimethacrylate (Bis-EMA) [42]. 2 mol% of camphorquinone (CQ) was used as a photosensitizer, and 2 mol% of *N, N*-dimethylaminoethyl methacrylate was used as reducing agent. Resins prepared from copolymerized Bis-GMA/TEGDMA showed a higher Young's modulus. Bis-GMA/UDMA and Bis-GMA/Bis-EMA resins were more flexible than Bis-GMA/TEGDMA resins and the former absorbed lower water amount and released higher unreacted monomers than the latter. The influence of the chemical structure of resins on their thermal degradation was studied by Achilias et al. based on resins comprised of bis-phenol A glycidyl dimethacrylate (Bis-GMA), bis-phenol A ethoxylated dimethacrylate (Bis-EMA), urethane dimethacrylate (UDMA), and triethylene glycol dimethacrylate (TEGDMA). Bis-GMA and Bis-EMA because of their rigid aromatic nuclei formed a more rigid network and decomposed at higher temperatures compared to that from TEGDMA and UDMA. Moreover, Bis-GMA is also characterized by strong hydrogen bonding ability that could be the reason for its high thermal stability [43]. The influence of curing rate on the mechanical properties of common dental resin Bis-GMA/TEGDMA was analyzed by Lovell et al. He showed that copolymer resins cured using UV and visible light exhibited similar glass transition and modulus irrespective of the method or rate of cure [44]. Yue et al. described two general strategies for the preparation of antimicrobial resins. In one strategy, positively charged monomers with appended alkyl chains possessing antimicrobial characteristics are directly copolymerized with resin components such as UDMA/GDMA (diurethane dimethacrylate/glycerol



Measurement Approaches for PAM

Microscopy: chemical atomic force microscopy, dynamic force microscopy, scanning transmission electron microscopy, scanning electron microscopy, aberration-corrected transmission electron microscopy, focused ion beam techniques, scanning near-field optical microscopy, scanning interferometric apertureless microscopy, photonic force microscopy

Spectral: Electron energy-loss spectroscopy, X-ray scattering, real-time infrared spectroscopy

Additional Common Tools: dynamic mechanical analysis, tensile/compression, rheometry, X-ray computed tomography

Looking Ahead Capabilities: Integrated approaches, in-situ measurements, data platforms, visualization, nanometer scales or less

FIGURE 13.4 Measurement approaches for PAM [11].

dimethacrylate) using photocuring. In the second strategy, they are prepolymerized as a linear chain and then added into the semi-interpenetrating polymer network using light-induced polymerization. The materials produced using both strategies have shown minimal bioactive leaching. Nevertheless, the polymer resin fabricated by the second strategy has shown the least leaching of positively charged bioactive moieties because of the hydrogen or covalent bond formation between the antimicrobial polymer and the cross-linked network. The fabricated antimicrobial resins can be used as luting cement, adhesive, or as composite for cavity restoration in dentistry [6].

13.4 Applications

In 1969, Close et al. first discovered photopolymers as a holographic recording material [45]. This is primarily a liquid state material that consists of a mixture of acrylamide, metal acrylate monomers, and a photocatalyst, methylene blue. A polyvinyl alcohol (PVA) binder when included changed the drying condition of the polymer layers, and the original system proposed by Close was modified by Sadlej and Smolinska [46]. In 1987, Calixto continued the work on acrylamide based systems. This material was formed and processed with an acrylamide monomer, triethylamine (TEA) as an electron donor, methylene blue (MB) photosensitizer, and PVA as a binder [47]. By changing the cross-linker, *N*,*N*′-(1,2-Dihydroxyethylene) bisacrylamide (DHEBA), the sensitivity of the acrylamide material for recording at 633 nm was improved by Blaya et al. in 1998 [48]. Zhao et al. proposed a hybrid material containing acrylamide and acrylic acid as monomers. Here methylene blue was used as the photosensitizer, TEA and *p*-toluenesulfonic acid as sensitizers, and gelatin as the binder, respectively [49].

Based on PVA and vinyl acetate sensitized with methylene blue, John et al. developed a new photopolymerizable recording media that have the capability to be erased. PVA and vinyl acetate at 2:1 ratio was obtained [50]. Diffraction efficiency of 6.3% was obtained at an exposure of 750 $\mathrm{mJ/cm^2}$. It was highly reusable and less toxic, thus the material was attractive. With a continuous fall in diffraction efficiency, the recorded gratings were found to remain in the material for 24 h. The values were recorded around the same point in the same film after 24 hours, to examine the reusability of the methylene blue PVA and vinyl acetate system. From the results, it was observed that the methylene blue PVA and vinyl acetate system could be reused multiple times. For hologram recording in the acrylamide-based photopolymer material layers, a combination of two multiplexing methods, peritrophic and angular multiplexing, was reported by Fernandez et al. In this study an optimized exposure schedule method was employed during the recordings which give out holograms with better uniform diffraction efficiency in thick material layers. From 60 holograms recorded, mean diffraction efficiencies of 1.8% were also obtained [51]. In another study, Jeong et al. introduced an epoxy-resin cross-linked matrix into an acrylamide-based photopolymer material to enhance the material's energetic sensitivity. By the additions of epoxy-resin-based matrix, diffraction efficiency near 92% and an energy sensitivity of $11.7 \times 10^{-3}\ \mathrm{cm^2/J}$ were achieved. It was found that the epoxy-resin-based cross-linked photopolymer with low cross-linking density had a positive effect on the energetic sensitivity without affecting and reducing both the diffraction efficiency and dimensional stability. The photopolymer with low cross-linking density could significantly enhance the energetic sensitivity [52]. In another study conducted in the same year, to reduce the depth variation of recording intensity in thick PVA/acrylamide photopolymer layers, Ling et al. used a triangle prism tilted at a certain low angle to the axis within the focus of a lens. For the modulated recording lights, mean diffraction efficiency of 9.5% was obtained. As a result of the reduction in the attenuation in the depth of light of the material, a larger dynamic range, $M = 9.2$ was obtained from the results [53].

Feng et al. developed biodegradable photocurable polyurethane resin loaded with graphene prepared by stereolithography (Fig. 13.5). The material exhibited excellent mechanical properties and could mimic porous bone structures which have a great potential in tissue engineering. The biggest advantage is that this resin had a relatively low viscosity (from 0.25 to 1 Pa s) and when graphene was added the viscosity was 0.847 Pa s which is ideal for SLA 3D printing. They prepared scaffolds of jawbone sternum with square and round architecture, respectively, and a gyroid scaffold made of nanocomposites was fabricated via an SLA AM mechanism [54].

In another 2020 study, a yellow-light emitter was combined with a blue light-emitting clear resin and a white light-emitting composite was produced by the stereolithography technique. Here a nanoconfinement process is employed on two fluorophores and the dilution effect of the dyes has a profound effect on the emission spectra. This is a one-pot facile technique aimed at converting UV into white light emission and has great implications in energy-saving applications [55]. In another study by Voet et al. homogeneous acrylate clear and renewable resins were prepared by a stereolithographic printing procedure. This method utilizes a simple strategy to produce

FIGURE 13.5 Graphene-reinforced nanocomposite gyroid scaffold for bone tissue engineering [54].

complicated 3D printed parts out of bio-based renewable polymers [56]. DMX-SL™ 100 is a resin, which is commonly used for producing parts that are highly tough and durable [57]. The DMX-SL 100 is durable and tough stereolithography resin, which is an efficient and comparatively cheap printing solution that produces a highly accurate structure with excellent surface finish and high detailing, thereby promoting better design flexibility for composite applications. The DMX-SL 100 has the ability to withstand high temperatures utilized in the process for composites manufacturing but has the ability to maintain its mechanical properties like flexural strength, elongation, and tear resistance [34]. These unique properties allow the mandrels to be removed from complex and convoluted geometries by an inherently dry process which is unique for a solid mandrel. Other process involves mixing the material in an acidic environment which directly affects the performance of the composite part. This is a one-of-a-kind material utilized in the industry as it can be easily and efficiently removed after the autoclave process, facilitating the better and more efficient production of intricate designed composite parts. This method of using three-dimensional printing to produce a sacrificial tooling is quite straightforward and can be fine-tuned by the user by employing multiple iterations.

Many important advances in the field of 3D printing have occurred in recent years, including the introduction of volumetric 3D printing to improve printing speed, composite 3D printing for the manufacture of piezoelectric products, and hydrogel frameworks that are strikingly identical to blood vessels. The number of printable materials has also expanded, enabling researchers to print a wide range of materials including live cells, polymer-changing modules, and even spacecraft-grade metals [58]. SLA clear resins are used to manufacture prototypes of extremely detailed, fully transparent headlights for aircraft [16]. Ma et al. [59] created a robotic-assisted in situ 3D bioprinting platform for regeneration of cartilages, where a six-degree-of-freedom (6-DOF) robot was implemented and a rapid calibration process of the tool center point (TCP) was built to optimize printing precision. The bio-ink was made up of 4-armed polyethylene glycol terminated with acrylate and methacrylate hyaluronic acid. To validate the printing efficiency, they undertook an in vitro procedure on a resin template, and an in vivo analysis on rabbits was performed to assess its potential for cartilage repair.

COVID-19 has renovated 3D printing while demonstrating its value and dramatically improving its uses to produce personal protective equipment for healthcare staff by technological institutions, researchers, universities, etc. The swift prototyping advancements which fall among the critical applications of 3D printing enabled face mask designs, components for ventilators, and even coronavirus nasal testing swabs to promptly be made available to the public. Rather than waiting for such health products and apparatuses to be bulk-produced abroad and then transported to local hospitals, 3D printing permitted machinery and parts to be fabricated on-demand and close [60].

13.5 Bio-based photopolymers

The effectiveness of AM employing renewable resources is pivotal in constructing fully compliant and competent products that are ecologically viable and economically feasible. The accessibility of renewable materials for AM is becoming exceedingly relevant to encourage the continuing changeover toward a circular economy [56,61]. It has been reported by Wu et al. that the inclusion of a portion of ester thiols and aliphatic polycarbonate alkyne in the photo resin composition is beneficial in having the ability to easily degrade 3D printed items hydrolytically [20]. The efficient development of complex structured prototypes from biopolymer-based acrylate photo resins, using an industrial SLA 3D printer, was reported by Voet and coworkers. The creation of high-viscosity resins resulted in prototypes with a better resolution possessing a detailed microarchitecture and superior coating finish, as compared to those commercially available nonrenewable resins [56]. The successful implementation of renewable, modified lignin containing photopolymer resins in an industrial stereolithography device was reported by Sutton et al. In contrast to commercial SLA resins, a fourfold increment in ductility was observed in cured sections with higher lignin concentrations. Modified lignin resins with excellent layer fusion, greater surface resolution, and optical transparency demonstrated outstanding print quality [61]. The commercially available bio-based compounds such as isobornyl methacrylate (IBOMA), tetrahydrofurfuryl acrylate (THFA), methacrylic ester (ME), tetrahydrofurfuryl methacrylate (THFA), and acrylated epoxidized soybean oil (AESO) were used to prepare solvent-free acrylate photo resins appropriate for use in DLP 3D printing technology (THFMA), with 75%–82% renewable carbon content demonstrating high printing accuracy and good adhesion between layers. In the prototyping of bio-based products, soybean oil derivatives have attracted tremendous interest. The significance of choosing soybean oil is that it is biocompatible and has reactive double bonds that are unsaturated, making it more feasible to work when compared to PCL and PLA. It can also be added into hydroxy and epoxy functionalities owing to the large proportion of unsaturated sites in acrylate, triglyceride, and methacrylate groups, culminating in its superior sensitivity in photo cross-linking reactions [8,62,63].

13.6 Opportunities and challenges

Contrasted to thermoplastics used by selective laser sintering and fused deposition modeling, thermosetting photopolymers used by stereolithography and PolyJet have relatively low temperatures of deflection. From such information, designers can select the types of material to adopt and also the resultant technology for printing for a particular application. While in one aspect, a particular material may be superior, at the same time could be inferior in another [28]. Since thermosetting resins are not capable of retaining their shape without being cross-linked or incorporated with excessive fillers, and cannot be extruded for printing once cross-linked, 3D printing of thermosetting polymers is limited to photopolymerization of customized photosensitive resins or extrusion of resins equipped with massive fragments of rheological modifiers (up to 20% by weight) [64]. Even though thiols demonstrate good potential as AM resin elements with less shrinkage stress and firm nature, drawbacks including inefficient storage consistency, foul odor, and lower final material modulus continue to be problems to tackle. Addition–fragmentation chain transfer (AFCT) reagents are scrutinized in photocurable compositions to recognize the correlation between well-designed polymer structure and enhanced material properties [18].

While handling hybrid (dual-cure) formulations, despite the benefits they offer, it has been discovered that the incongruence of the two monomers can pose challenges for the final configuration and features of the resulting resins. Such a composition is fairly archetypal, but changes in the formulation can be rendered for some requirements in order to change cross-link density and thereby affect their mechanical properties or minimize water absorption [65]. For parts originating from photosensitive materials, an infill density lesser than 100% is not feasible since any overhanging attributes of the parts must be stabilized during the fabrication process to avoid them from breaking under their own weight [66,67]. Although 3D printing/stereolithography is the quickest developing photopolymer industry, visual appearance, wear resistance, wet resilience, and dimensional precision are the key prevailing technical constraints limiting the advancement of 3D printing to practical component output [15].

A limitation of photopolymer technologies is the limited range of available materials, which should be photocurable resins with optical transparency. The biocompatibility and general safety of the resins is also a major concern as some of the monomers can cause serious environmental problems. Hence more work should focus on bringing new functionality resins that are nontoxic alongside maintaining sufficient mechanical stability.

References

[1] B. Joseph, N. Ninan, R.M. Visalakshan, C. Denoual, R. Bright, N. Kalarikkal, Y. Grohens, K. Vasilev, S. Thomas, Insights into the biomechanical properties of plasma treated 3D printed PCL scaffolds decorated with gold nanoparticles, Compos. Sci. Technol. 202 (2021) 108544, https://doi.org/10.1016/j.compscitech.2020.108544.

[2] Wikipedia®, Photopolymer, https://en.wikipedia.org/wiki/Photopolymer (Accessed 18 June 2021).

[3] A. Bagheri, J. Jin, Photopolymerization in 3D printing, ACS Appl. Polym. Mater. 1 (2019) 593—611, https://doi.org/10.1021/acsapm.8b00165.

[4] M. Layani, X. Wang, S. Magdassi, Novel materials for 3D printing by photopolymerization, Adv. Mater. 30 (2018).

[5] M. Motavalli, C. Czaderski, A. Schumacher, D. Gsell, Fibre reinforced polymer composite materials for building and construction, in: Textiles, Polymers and Composites for Buildings, Elsevier Ltd., 2010, ISBN 9781845693978, pp. 69—128.

[6] S.H. Lim, H. Kathuria, M.H.B. Amir, X. Zhang, H.T.T. Duong, P.C.L. Ho, L. Kang, High resolution photopolymer for 3D printing of personalised microneedle for transdermal delivery of anti-wrinkle small peptide, J. Contr. Release 329 (2020), https://doi.org/10.1016/j.jconrel.2020.10.021.

[7] J. Li, M. Pumera, 3D printing of functional microrobots, Chem. Soc. Rev. 50 (2021), https://doi.org/10.1039/D0CS01062F.

[8] M. Lebedevaite, V. Talacka, J. Ostrauskaite, High biorenewable content acrylate photocurable resins for DLP 3D printing, J. Appl. Polym. Sci. 138 (2021), https://doi.org/10.1002/app.50233.

[9] V.S.D. Voet, G.H.M. Schnelting, J. Xu, K. Loos, R. Folkersma, J. Jager, Stereolithographic 3D printing with renewable acrylates, JoVE 2018 (2018) e58177, https://doi.org/10.3791/58177.

[10] K.S. Reddy, S. Dufera, Additive manufacturing technologies, Int. J. of Man. Inf. Tech. Eng 4 (7) (2016) 89—112.

[11] C. Higgins, J. Killgore, D. Poster, Report from the photopolymer additive manufacturing workshop: roadmapping a future for stereolithography, inkjet, and beyond, in: Proceedings of the NIST Special Publication 1500-17, 2021, pp. 1—79.

[12] Y. Gao, L. Xu, Y. Zhao, Z. You, Q. Guan, 3D printing preview for stereo-lithography based on photopolymerization kinetic models, Bioact. Mater. 5 (2020) 798—807, https://doi.org/10.1016/j.bioactmat.2020.05.006.

[13] G. Taormina, C. Sciancalepore, M. Messori, F. Bondioli, 3D printing processes for photocurable polymeric materials: technologies, materials, and future trends, J. Appl. Biomater. Funct. Mater. 16 (2018) 151—160, https://doi.org/10.1177/2280800018764770.

[14] G.D. Goh, S. Agarwala, G.L. Goh, V. Dikshit, S.L. Sing, W.Y. Yeong, Additive manufacturing in unmanned aerial vehicles (UAVs): challenges and potential, Aero. Sci. Technol. 63 (2017) 140—151.

[15] A. Della Bona, V. Cantelli, V.T. Britto, K.F. Collares, J.W. Stansbury, 3D printing restorative materials using a stereolithographic technique: a systematic review, Dent. Mater. 37 (2020) 336—350.

[16] J.C. Najmon, S. Raeisi, A. Tovar, Review of additive manufacturing technologies and applications in the aerospace industry, in: Additive Manufacturing for the Aerospace Industry, Elsevier Inc., 2019, ISBN 9780128140635, pp. 7—31.

[17] C. Wang, W. Huang, Y. Zhou, L. He, Z. He, Z. Chen, X. He, S. Tian, J. Liao, B. Lu, et al., 3D printing of bone tissue engineering scaffolds, Bioact. Mater. 5 (2020) 82—91, https://doi.org/10.1016/j.bioactmat.2020.01.004.

[18] S.C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mulhaupt, Polymers for 3D printing and customized additive manufacturing, Chem. Rev. 117 (2017) 10212—10290.

[19] G.K. Awari, C.S. Thorat, V. Ambade, D.P. Kothari, Additive Manufacturing and 3D Printing Technology: Principles and Applications, CRC Press, 2021.

[20] Y. Wu, M.C. Simpson, J. Jin, Fast hydrolytically degradable 3D printed object based on aliphatic polycarbonate thiol-yne photoresins, Macromol. Chem. Phys. (2021) 2000435, https://doi.org/10.1002/macp.202000435.

[21] C.J. Thrasher, J.J. Schwartz, A.J. Boydston, Modular elastomer photoresins for digital light processing additive manufacturing, ACS Appl. Mater. Interfaces 9 (2017) 39708—39716.

[22] Y.H. Lee, J.B. Lee, W.Y. Maeng, Y.H. Koh, H.E. Kim, Photocurable ceramic slurry using solid camphor as novel diluent for conventional digital light processing (DLP) process, J. Eur. Ceram. Soc. 39 (2019) 4358—4365, https://doi.org/10.1016/j.jeurceramsoc.2019.05.069.

[23] S. Kumar, Selective laser sintering/melting, in: Comprehensive Materials Processing, vol. 10, Elsevier Ltd, 2014, ISBN 9780080965338, pp. 93—134.

[24] K. Mohamed, Nanoimprint lithography for nanomanufacturing, in: Comprehensive Nanoscience and Nanotechnology, vols. 1—5, Elsevier, 2019, ISBN 9780128122952, pp. 357—386.

[25] A.T. Cullen, A.D. Price, Digital light processing for the fabrication of 3D intrinsically conductive polymer structures, Synth. Met. 235 (2018), https://doi.org/10.1016/j.synthmet.2017.11.003.

[26] T. Chartier, C. Dupas, P.M. Geffroy, V. Pateloup, M. Colas, J. Cornette, S. Guillemet-Fritsch, Influence of irradiation parameters on the polymerization of ceramic reactive suspensions for stereolithography, J. Eur. Ceram. Soc. 37 (2017), https://doi.org/10.1016/j.jeurceramsoc.2017.05.050.

[27] A.D. Benjamin, R. Abbasi, M. Owens, R.J. Olsen, D.J. Walsh, T.B. Lefevre, J.N. Wilking, Light-based 3D printing of hydrogels with high-resolution channels, Biomed. Phys. Eng. Express 5 (2019), https://doi.org/10.1088/2057-1976/aad667.

[28] J.R.C. Dizon, A.H. Espera, Q. Chen, R.C. Advincula, Mechanical characterization of 3D-printed polymers, Addit. Manuf. 20 (2018) 44—67, https://doi.org/10.1016/j.addma.2017.12.002.

[29] K.S. Lee, R.H. Kim, D.Y. Yang, S.H. Park, Advances in 3D nano/microfabrication using two-photon initiated polymerization, Prog. Polym. Sci. 33 (2008).

[30] S. Waheed, J.M. Cabot, N.P. Macdonald, T. Lewis, R.M. Guijt, B. Paull, M.C. Breadmore, 3D printed microfluidic devices: enablers and barriers, Lab Chip 11 (2016).

[31] J. Zhang, P. Xiao, 3D printing of photopolymers, Polym. Chem. 13 (2018).

[32] T.J. Trentler, J.E. Boyd, V.L. Colvin, Epoxy resin — photopolymer composites for volume holography, Chem. Mater. 12 (2000), https://doi.org/10.1021/cm9908062.

[33] P. Vinogradov, 3D printing in medicine: Current challenges and potential applications, Printing Technology in Nanomedicine, Elsevier Inc, Missouri, 2019, p. 1.

[34] C. Zhang, T.F. Garrison, S.A. Madbouly, M.R. Kessler, X. Huang, X. Yang, H. Liu, S. Shang, Z. Cai, K. Wu, et al., Photopolymers in 3D printing applications, Prog. Org. Coating 74 (2019) 297–316.

[35] S.T. Spence, D.R. Smalley, U.S. Patent No. 5,182,056, U.S. Patent and Trademark Office, Washington, DC, 1993.

[36] B. Modrek, B. Parker, S. T. Spence, U.S. Patent No. 5,164,128, U.S. Patent and Trademark Office, Washington, DC, 1992.

[37] Z. Yang, J. Shan, Y. Huang, X. Dong, W. Zheng, Y. Jin, W. Zhou, Preparation and mechanism of free-radical/cationic hybrid photosensitive resin with high tensile strength for three-dimensional printing applications, J. Appl. Polym. Sci. 138 (2021) 49881, https://doi.org/10.1002/app.49881.

[38] A. L. Coats, J. P. Harrison, J. S. Hay, M. J. Ramos, U.S. Patent No. 7,211,368, U.S. Patent and Trademark Office, Washington, DC, 2007.

[39] D. Wang, K. Wu, G. Li, L. Wang, The viscoelastic mechanical property and constitutive models of 3D printed photopolymer, Rapid Prototyp. J. 27 (2021), https://doi.org/10.1108/RPJ-07-2020-0163.

[40] M. Monzón, Z. Ortega, A. Hernández, R. Paz, F. Ortega, Anisotropy of photopolymer parts made by digital light processing, Materials 10 (2017), https://doi.org/10.3390/ma10010064.

[41] A. Tahayeri, M.C. Morgan, A.P. Fugolin, D. Bompolaki, A. Athirasala, C.S. Pfeifer, J.L. Ferracane, L.E. Bertassoni, 3D printed versus conventionally cured provisional crown and bridge dental materials, Dent. Mater. 34 (2018), https://doi.org/10.1016/j.dental.2017.10.003.

[42] I. Sideridou, V. Tserki, G. Papanastasiou, Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins, Biomaterials 24 (2003), https://doi.org/10.1016/S0142-9612(02)00380-0.

[43] D.S. Achilias, M.M. Karabela, I.D. Sideridou, Thermal degradation of light-cured dimethacrylate resins, Thermochim. Acta 472 (2008) 74–83, https://doi.org/10.1016/j.tca.2008.02.004.

[44] L.G. Lovell, H. Lu, J.E. Elliott, J.W. Stansbury, C.N. Bowman, The effect of cure rate on the mechanical properties of dental resins, Dent. Mater. 17 (2001), https://doi.org/10.1016/S0109-5641(01)00010-0.

[45] D.H. Close, A.D. Jacobson, J.D. Margerum, R.G. Brault, F.J. McClung, Hologram recording on photopolymer materials, Appl. Phys. Lett. 14 (1969), https://doi.org/10.1063/1.1652756.

[46] N. Sadlej, B. Smolinska, Stable photo-sensitive polymer layers for holography, Opt Laser. Technol. 7 (1975), https://doi.org/10.1016/0030-3992(75)90056-0.

[47] S. Calixto, Dry polymer for holographic recording, Appl. Opt. 26 (1987), https://doi.org/10.1364/ao.26.003904.

[48] S. Blaya, R. Mallavia, L. Carretero, A. Fimia, R.F. Madrigal, Highly sensitive photopolymerizable dry film for use in real time holography, Appl. Phys. Lett. 73 (1998), https://doi.org/10.1063/1.122227.

[49] F. Zhao, E.E.E. Frietman, X. Li, Novel type of red-sensitive photopolymer system for optical storage, in: Proceedings of the Advanced Optical Memories and Interfaces to Computer Storage, 1998.

[50] B.M. John, M. Ushamani, R. Joseph, K. Sreekumar, C.S. Kartha, Reusable recording medium based on MBPVA and vinyl acetate, J. Mod. Opt. 53 (2006), https://doi.org/10.1080/09500340500402173.

[51] E. Fernández, M. Ortuño, S. Gallego, C. García, A. Beléndez, I. Pascual, Comparison of peristrophic multiplexing and a combination of angular and peristrophic holographic multiplexing in a thick PVA/acrylamide photopolymer for data storage, Appl. Opt. 46 (2007), https://doi.org/10.1364/AO.46.005368.

[52] Y.-C. Jeong, S. Lee, J.-K. Park, Holographic diffraction gratings with enhanced sensitivity based on epoxy-resin photopolymers, Opt Express 15 (2007), https://doi.org/10.1364/oe.15.001497.

[53] F. Ling, B. Tong, S. Jiang, B. Wang, Y. Zhang, Optimization of holographic storage with modulated recording beams in a thick polyvinyl alcohol/acrylamide photopolymer, J. Opt. Soc. Am. A 24 (2007), https://doi.org/10.1364/josaa.24.001945.

[54] Z. Feng, Y. Li, L. Hao, Y. Yang, T. Tang, D. Tang, W. Xiong, Graphene-reinforced biodegradable resin composites for stereolithographic 3D printing of bone structure scaffolds, J. Nanomater. 2019 (2019), https://doi.org/10.1155/2019/9710264.

[55] A.K. Chaudhari, J.C. Tan, Dual-guest functionalized zeolitic imidazolate framework-8 for 3D printing white light-emitting composites, Adv. Opt. Mater. 8 (2020), https://doi.org/10.1002/adom.201901912.

[56] V.S.D. Voet, T. Strating, G.H.M. Schnelting, P. Dijkstra, M. Tietema, J. Xu, A.J.J. Woortman, K. Loos, J. Jager, R. Folkersma, Biobased acrylate photocurable resin formulation for stereolithography 3D printing, ACS Omega 3 (2018) 1403–1408, https://doi.org/10.1021/acsomega.7b01648.

[57] T. Wohlers, T. Gorne, History of additive manufacturing, Wohlers Report (2014) pp. 1–34.

[58] I. Karakurt, L. Lin, 3D printing technologies: techniques, materials, and post-processing, Curr. Opin. Chem. Eng. 28 (2020) 134–143.

[59] K. Ma, T. Zhao, L. Yang, P. Wang, J. Jin, H. Teng, D. Xia, L. Zhu, L. Li, Q. Jiang, X. Wang, Application of robotic-assisted in situ 3D printing in cartilage regeneration with HAMA hydrogel: An in vivo study. J. Adv. Res. 23 (2020) 123–132.

[60] M. Attaran, 3D printing role in filling the critical gap in the medical supply chain during COVID-19 pandemic, Am. J. Ind. Bus. Manag. 10 (2020) 988–1001, https://doi.org/10.4236/ajibm.2020.105066.

[61] J.T. Sutton, K. Rajan, D.P. Harper, S.C. Chmely, Lignin-containing photoactive resins for 3D printing by stereolithography, ACS Appl. Mater. Interfaces 10 (2018), https://doi.org/10.26434/chemrxiv.6820229.v3.

[62] J.Z. Manapat, Q. Chen, P. Ye, R.C. Advincula, 3D printing of polymer nanocomposites via stereolithography, Macromol. Mater. Eng. 302 (2017) 1600553.

[63] J. Guit, M.B.L. Tavares, J. Hul, C. Ye, K. Loos, J. Jager, R. Folkersma, V.S.D. Voet, Photopolymer resins with biobased methacrylates based on soybean oil for stereolithography, ACS Appl. Polym. Mater. 2 (2020) 949–957, https://doi.org/10.1021/acsapm.9b01143.

[64] M. Mahmoudi, S.R. Burlison, S. Moreno, M. Minary-Jolandan, Additive-free and support-free 3D printing of thermosetting polymers with isotropic mechanical properties, ACS Appl. Mater. Interfaces 13 (2021), https://doi.org/10.1021/acsami.0c19608.

[65] Y. Cai, J.L. Jessop, Decreased oxygen inhibition in photopolymerized acrylate/epoxide hybrid polymer coatings as demonstrated by Raman spectroscopy, Polymer 47 (2006) 6560–6566.

[66] I. Gibson (Ed.), Advanced Manufacturing Technology for Medical Applications: Reverse Engineering, Software Conversion and Rapid Prototyping, John Wiley & Sons, 2006.

[67] Y. Li, B.S. Linke, H. Voet, B. Falk, R. Schmitt, M. Lam, Cost, sustainability and surface roughness quality – a comprehensive analysis of products made with personal 3D printers, CIRP J. Manuf. Sci. Technol. 16 (2017) 1–11, https://doi.org/10.1016/j.cirpj.2016.10.001.

C H A P T E R

14

Polymers in printing filaments

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14.1 3D printing filaments − introduction

Extrusion-based processes are among the most widely used additive manufacturing (AM) technologies, currently dominated by fused deposition modeling (FDM) [1]. This technique developed in the early 1990s uses preformed polymer in the form of continuous filament as the building material. Commercial 3D printing filaments are manufactured by melt extrusion process. Polymer pellets are melted through applied heat and friction, molted polymer is then forced under high pressure through a small orifice, and after flowing out from orifice the molten polymer yet solidifies in the air or water into the solid filament. The filament is cooled down according to a predefined temperature profile. The final diameter is determined with the drawing using different force and speed. Filaments are available in two standard diameters: 1.75 and 2.85/3 mm. In smaller-scale systems, the continuous filament is simply a loose coil, while in larger manufacturing systems, it is coiled inside a cartridge to supply the system [1].

FDM is limited to extrusion of thermoplastic polymer at elevated temperature. The thermoplasticity of the filament is an essential property for FDM technology, which allows the filament to fuse together during printing and then to solidify at room temperature after printing. The filament itself must have good mechanical and thermal stability because of tension, compression, and heating acting on it in the feeding and melting steps of FDM process [2]. Mechanical properties are highly depended from the type of polymer and 3D printing process parameters. Due to the inherent lack of strength and functionality of most thermoplastic polymers used by FDM the applications of printed objects are limited. The inferior mechanical properties of 3D-printed polymers can be overcome, with development of new materials, blends, and composites [3].

The most common materials used in FDM are amorphous thermoplastics, with acrylonitrile butadiene styrene (ABS) being the most common. Besides, ABS, polylactide (PLA), polyamide (PA), and polycarbonate (PC) are most frequently used [4]. Higher-grade devices can also process high-performance materials, like polyphenylsulfone (PPSU). Polymers from the whole range of the “pyramid of polymeric materials” are used, ranging from commodity polymers with limited properties, engineering polymers to high-performance polymers with excellent mechanical properties, chemical and thermal stability. Due to the greater materials tolerance in FDM as compared with SLS processes, also recycled commodity polymer stocks can be considered for use [5].

The relatively straightforward “melt-apply-solidify” FDM process has enabled that this technique is by far the most common version of 3D printing and it represents the vast majority of consumer-based low cost devices [6]. From the study of Wittbrodt et al. [7] it can be concluded that RepRap was an economically attractive investment for the average US household already in 2013. It appears that open-source 3D printers will become mass-market mechatronic devices. With this, the need for broader specter of filament properties will initiate the development of new filament types, mainly composites [7].

As the traditional area of prototyping is expanding more and more into manufacturing, this induces a growth of the 3D printing industry and promotes development of 3D printing filaments with improved properties [8]. With the progress on the machine side, improved reliability, increased build speed, and intuitive user interfaces, the range of applications for 3D-printed objects keeps growing steadily. Besides that, there is a lot of development in materials to expand the scope of manufacturing [9].

Polymers for 3D Printing
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14.2 Commodity polymers

14.2.1 Polyolefins

14.2.1.1 Development

Polyolefin belongs to the commodity thermoplastic polymer. Polyolefins are class of polymers formed by the polymerization of olefin monomer units, hydrocarbons whose molecules contain a pair of carbon atoms linked together by a double bond [10]. The most common polyolefins are polypropylene (PP) and polyethylene (PE), together making around half of plastic production [11].

PE was first synthesized in 1898 by accident while heating diazomethane [12]. The first industrially practical synthesis was discovered in 1933 and a reproducible high-pressure synthesis in 1935 at the ICI works in England. This was the basis for industrial low-density polyethylene (LDPE) production, beginning in 1939 [13]. In 1944 Bakelite Corporation (US) and DuPont (US) began large-scale commercial production under license from ICI. The breakthrough in the commercial production was the development of catalyst that enabled the polymerization at mild temperatures and pressures [14]. An efficient stereospecific polymerization procedure was developed by Karl Ziegler and Giulio Natta in the 1950s, which permitted the synthesis of unbranched, high-molecular-weight polyethylene (HDPE) [15]. In 1956 they started the production of HDPE, and by the end of the 1950s both the Phillips- and Ziegler-type catalysts were being used for HDPE production. Catalytic systems based on metallocenes were reported in 1976 [16]. The Ziegler- and metallocene-based catalysts become the basis for the wide range of PE resins available today.

PP was first polymerized by Robert Banks and J. Paul Hogan at Phillips Petroleum Company (US) in 1951 [17]. Isotactic PP (i-PP) was discovered in 1954 by Natta, who used new catalysts developed by Ziegler that enabled configurational control of polymers from terminal alkenes like propene [18]. This led to first large-scale commercial production of PP by the Italian firm Montecatini in 1957 [19]. In the 1980s, a new generation of catalyst called metallocene was launched. The new catalyst provided the opportunity to tailor the polymer structure and the tacticity of PP resins [20].

14.2.1.2 Chemical structure and synthesis

The IUPAC nomenclature term of polyolefin is poly(alkene). They consist only of carbon and hydrogen atoms and they are nonaromatic. PE is produced by the polymerization of ethylene (ethene), a gaseous hydrocarbon, usually produced from petrochemical sources, or generated by dehydration of ethanol [21]. Among several types of PE the most used are low-density PE (LDPE) and high-density PE (HDPE). The chemical formula of PE is $(C_2H_4)_n$. The IUPAC source-based name is polyethene, and the structure-based name is poly(methylene) [22]. Molecular weight of repeat unit is 28.05 g/mol [23].

PP is produced from propylene, a gaseous compound obtained by the thermal cracking of ethane, propane, butane, and the naphtha fraction of petroleum [24]. The chemical formula of PP is $(C_3H_6)_n$. IUPAC name for monomer is Prop-1-ene and for polymer poly(propene), and the structure-based name is poly(1-methylethane-1,2-diyl). Molecular weight of repeat unit is 42.08 g/mol [25]. Repeat units of PE and PP are shown in Fig. 14.1.

Many processes have been developed for the polymerization of olefins. They differ in the physical state of the reactor media and in the mechanical operation of the unit [10]. HDPE is produced by stereospecific catalytic polymerization of ethylene. Three types of catalysts are used: a Ziegler–Natta organometallic catalyst (titanium compounds with an aluminum alkyl), a Phillips-type catalyst, an inorganic compound (chromium(VI) oxide deposited on silica), or a metallocene catalyst [21]. These catalysts prefer the formation of free radicals at the ends of the growing PE molecules; ethylene monomers add to the ends of the molecules causing the growth of a linear chain. By choosing catalysts and reaction conditions, the amount of branching and molecular weight of polymer can be controlled [15]. All mentioned processes operate at relatively low pressures (10–80 atm) in the temperature range between 177 and 216°C. In all three processes hydrogen is mixed with the ethene to control the chain length of the polymer [26].

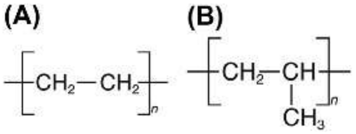


FIGURE 14.1 Repeat units of: (A) PE, (B) PP.

HDPE can be produced in either slurry (suspension), solution, or gas phase reactors [27]. In the slurry process a mixture of hydrogen and ethene is passed under pressure into the slurry containing catalyst. The polymerization reaction takes place in a large loop reactor or continuous stirred tank reactor. Solvent is evaporated from polymer, after polymer/diluent separation, drying, and ethene removal follows, and finally HDPE polymer is converted to pellets [26]. In the solution process the polymer is obtained in a similar way to the slurry method. Ethene and hydrogen are fed under pressure into a solution of catalyst in a hydrocarbon. The polymer created is in the liquid phase. It is very viscous and for this reason a high-molecular-weight PE can't be obtained. At the gas phase process a mixture of ethene and hydrogen is passed over a Phillips catalyst in a fixed bed reactor. Ethene polymerizes to form grains of HDPE, suspended in the flowing gas. After polymer/reactant separation the PE powder is fed to powder silos and then converted into pellets [26].

PP is produced by the chain-growth polymerization of propene by Ziegler–Natta polymerization and by metallocene catalysis polymerization [28]. In the polymer, a pendant methyl group ($-CH_3$) is attached to alternate carbon atoms in the backbone of PP polymer chain. The methyl groups can adopt different spatial arrangements in relation to the carbon chain, resulting in different forms: isotactic, syndiotactic, and atactic. As the methyl group is in isotactic propylene consistently located at the same side, it forces the macromolecule in a helical shape [29]. Isotactic PP (i-PP) is produced at low temperatures and pressures, using Ziegler–Natta catalysts. The use of metallocene catalysts, i.e., catalysts with a single polymerization center on the metal, promotes the formation of polymers of homogeneous structure [30]. This results in precise control over molecular architecture for highly tailored polymers, improved processing, and properties of resins.

Polymerization of propylene through action of the metallocene or the titanium Ziegler–Natta catalyst gives an isotactic product; whereas, a vanadium-based Ziegler–Natta or a special class of metallocene catalysts gives a syndiotactic product [15]. Commercially available PP is usually in isotactic form, with an isotactic index between 90% and 95%. The industrial production processes of i-PP are gas phase polymerization, bulk polymerization, and slurry polymerization, with mainly gas-phase or bulk reactor systems applied [31]. Polymerization process is taking place either in a gas-phase (fluidized bed or stirred reactor) or a liquid-phase process (slurry or solution). The gas-phase polymerization is economical and flexible and can accommodate a large variety of catalysts. It is the most common technology in modern PP production plants [32].

14.2.1.3 Characteristics

A large number of end-use applications for polyolefins are possible because of the ability to tailor grades with specific properties and additives during manufacture. Their easy processability and low price in combination with their good chemical and physical properties makes them the most popular resins [33].

PE is the largest volume among polyolefins. A variety of different grades are commercially available, which differ in molecular weight, crystallinity (density), and branching [33]. At HDPE the poly(ethene) molecules can fit closer together, which leads to strong intermolecular bonds, making the material stronger, denser, and more rigid than LDPE [26]. It is also harder and more opaque and can withstand higher temperatures (120°C for short periods) and has good low temperature toughness (to −60°C). HDPE is lightweight material, and is known for its large strength-to-density ratio. It is flexible, translucent/waxy, resistant to moisture, shows good chemical resistance, impermeability, and impressive electrical insulating properties [34,35]. Benefits of HDPE are recyclability; it is hygienic and FDA-approved material.

PP is with the density of 0.904–0.908 g/cm^3 one of the lightest polymer among all commodity plastics. PP is a strong, lightweight thermoplastic that offers outstanding toughness, rigidity, tear resistance, and resistance to thermal deformation. It has good impact strength, is flexible (even at low temperatures), and possesses good fatigue resistance. It is very resistant to absorbing moisture, can be steam-sterilized or autoclaved without damage, and resists stress-cracking when subjected to most chemical tests. PP is a good electrical insulator [36,37]. It has excellent resistance to diluted and concentrated acids, alcohols, and base and good resistance to aldehydes, esters, aliphatic hydrocarbons, and ketones. PP retains mechanical and electrical properties at elevated temperatures, in humid conditions, and when submersed in water. It is a water-repellent plastic. PP has a high thermal expansion coefficient which limits its high temperature applications and tends to fail under mechanical and thermal stress [38].

Besides poor heat resistance, HDPE and PP also have poor weathering resistance and are susceptible to UV degradation and to oxidation. They have poor resistance to chlorinated solvents and aromatics and are flammable [39,40]. PP is known to be difficult to paint as it has poor bonding properties [38].

HDPE and PP have similar chemical and physical properties, with some differences. PP is stronger, stiffer, harder, is more rigid, and has better resistance to fatigue. PP softens at higher temperatures than PE; its melting point is approximately at 170°C. It is slightly more prone to oxidation than PE unless appropriate stabilizers and

TABLE 14.1 Typical properties of generic HDPE and PP polymers.

	HDPE	PP
Density (g/cm^3)	0.924–0.980	0.898–0.950
Melt flow rate (MFR) (g/10 min)	0.03–10	0.25–45
Water absorption: 23°C, 50% RH (%)	0.01–0.011	0.01–0.1
Water absorption: 24 h, immersed (%)	0.01–0.1	0.01–0.16
Tensile strength: Yield (MPa)	20.5–31.1	29.5–40.5
Tensile strength: Break (MPa)	13.6–36.1	19.0–26.5
Tensile elongation: Yield (%)	3–23	6.5–11
Tensile elongation: Break (%)	5–1000	1–510
Tensile modulus (GPa)	0.79–1.38	1.21–1.92
Flexural strength (MPa)	19.9–32.0	17–50
Flexural modulus (GPa)	0.76–1.40	1.17–1.94
Charpy notched impact strength (kJ/m^2)	2.9–27.3	1–5.46
Notched izod impact (kJ/m^2)	1.9–19.1	2–4
Rockwell hardness	45–60	89–112
Coefficient of friction	0.2–0.25	0.1–0.17
Deflection temperature under load: 0.45 MPa (°C)	65–95	79–106
Vicat softening temperature (°C)	65.5–129.5	88.3–157.2
Melting temperature (°C)	126–136	160–170
Thermal conductivity (W/mK)	0.403	0.202–0.4
Surface resistivity (Ohm)	$1.6\cdot10^{2}$–$2.5\cdot10^{15}$	10^{2}–10^{15}
Volume resistivity (Ohm•cm)	20–$2.5\cdot10^{15}$	10^{13}–10^{15}
Dielectric constant	2.32–2.5	2.25–2.5
Gloss (%)	5–120	85–111
Haze (%)	4.95–79.1	0.1–4.2

Adapted from Refs. [44,45].

antioxidants are added [24,41]. PP exhibits a high resistance to cracking, acids, organic solvents, and electrolytes, and is more resistant to chemicals and organic solvents compared to PE. PP is also lighter in weight, and has higher glass transition (Tg) and melting temperature (Tm) and good dielectric properties. PE stands up better in cold temperatures, particularly when using it as signs, and is a good electrical insulator. PE is sturdy as compared to PP, is more susceptible to stress cracking, and has high mold shrinkage. PE is inert, translucent and creates a lower static charge than PP [38,41,42].

An inherent characteristic common to all polyolefins is a nonpolar, nonporous, low-energy surface that is not receptive to inks, and lacquers without special oxidative pretreatment. Polyolefins have also some other limitations, such as poor temperature capability and poor weathering/UV resistance. PP can be compounded with fillers and fiber reinforcements to produce properties similar to thermoplastic engineering resins [43]. Typical properties of generic HDPE and PP polymers are presented in Table 14.1.

14.2.1.4 *Processing*

Polyolefins can be processed by thermoplastic-processing methods such as injection molding, blow molding, extrusion, and thermoforming [33]. They are the most widely used plastics for film extrusion [37].

HDPE favored for its strength, low cost, and impact resistance can be molded into a variety of shapes and products. Low cost of the material makes it an excellent material for disposable and recyclable industrial product

TABLE 14.2 Processing conditions for extrusion of HDPE and PP.

	HDPE	PP
Predrying	Not required	Not required
Melt temperature (°C)	180–205	200–250
Compression ratio	3:1	3:1
Screw design (L/D ratio)	25–30	25–30

Adapted from Refs. [48,49].

applications. Its comparative low density enables more volume of plastic to be processed [35]. HDPE can be molded in standard single-stage screw molding equipment. Best results are obtained when HDPE is molded at temperatures ranging from 204 up to 221°C, depending on melt-flow rate of polymer. If temperature is to high problems, for example, excessive flashing and burning, shrink phenomena and void formation can appear. Too low temperature can promote flow marks, weld lines, poor surfaces, lamination, short shots, and undesirable molded-in stresses [46].

Excellent thermal stability of PE enables processing over a wide temperature range without thermal degradation. Processes using HDPE are extrusion blow molding, coextrusion, and monofilament, sheet, film, profile and pipe extrusion. Extrusion blow molding as well as profile and pipe extrusion require good melt strength. Depending on the process, the temperature has to be modified to optimize the extrusion process being used [47]. HDPE resins for film extrusion are beside ordinary grades tailored to meet requirements for different applications, such as high stress cracking HDPE, high moisture barrier HDPE [37].

Most typically PP products are manufactured by extrusion blow molding, injection molding, and common extrusion methods for production of melt-blown and spun-bond fibers, continuous filaments, cast films, oriented and biaxially oriented films, and sheets [36]. PP is used in injection molding because of its good mold-in capability, low cost, and good properties, such as excellent moisture and chemical resistance and excellent impact strength. PP is easy to mold, and it flows very well because of its low melt viscosity [50]. Extrusion is the most popular process for forming PP. The extrusion process for manufacturing films/filaments can be briefly described in few steps: polymer melting in the extruder, extrusion through spinneret holes or slot-type die, quenching the film/filaments, drawing (finish application), and take-up (cutting/winding). For general extrusion, the temperature range from feed throat to front is 199–232°C, while cast film and fiber/filament extrusion require higher temperatures [36]. PP viscosity is more shear than temperature dependent. It has good melt strength, low processing temperature, and a large processing window [47]. Processing conditions for extrusion of HDPE and PP are given in Table 14.2.

Many physical finishing techniques can also be used on PP, such as machining, hot stamp printing, and vacuum metalizing. Surface treatments, such as gas flame, corona discharge, or plasma treatment, can be applied in order to promote adhesion of printing ink and paints [36].

14.2.1.5 Applications

PE is the most used plastic worldwide, and PP is the second-most widely produced commodity plastic. A high strength-to-density ratio, good mechanical properties, and versatility make HDPE very popular in a wide array of industries, specifically for packaging and assembly. Major use is in blow-molding and injection molding applications. HDPE is used in several packaging applications including crates, trays, bottles for milk and fruit juices, caps for food packaging, jerry cans, drums, industrial bulk containers, etc. It is used as film for food packaging and shopping bags. Several household/consumer goods, such as garbage containers, housewares, ice boxes, toys, etc., are made from HDPE. Other applications of HDPE include industrial and decorative textiles, automotive, pipes and fittings, and 3D printing [42,51].

PP is widely used in various applications: flexible and rigid packaging, consumer goods, for automotive, medical, textiles, and industrial applications. Cast, oriented, and bioriented films are used in food packaging, confectioneries, agriculture, consumer products, materials handling, including stretch wrap and shrink wrap, merchandise, electronic industry films, graphic arts applications, etc. [37,38]. Good barrier properties (low water uptake, low moisture–vapor transmission), high strength, excellent optical clarity, good surface finish, and low cost make PP ideal for flexible and rigid packaging. PP is blow molded to produce crates, bottles, pots, and injection molded to produce containers, caps and closures, etc. [38]. Reusable and collapsible/stackable crates are ideal for Just-in-Time (JIT) storage solutions. PP is found in several household products and consumer goods applications and other "durable" items for home, garden, or leisure use, including translucent parts, housewares, furniture, appliances, luggage, toys, etc. [29,38]. Due to its low cost, outstanding chemical and mechanical properties, processability, and moldability PP is used for automotive parts and interiors [38]. PP fiber and filament are used in industrial textiles, also in apparel. End products are carpets, upholstery fabrics, industrial fabrics, geotextiles, disposable fabrics, woven sacks, twine, rope, cord, tape, and strapping [52]. PP rope and twine are very strong and moisture resistant very suitable for marine applications. PP is used in various medical applications due to high chemical and bacterial resistance and resistance to steam sterilization [38]. High tensile strength, resistance to high temperatures, and corrosion resistance make PP suitable candidate for industrial sector to produce extruded and injection molded products, such as acid and chemical tanks, sheets, pipes, and returnable transport packaging (RTP) [29,38].

14.2.1.6 Recycling

Polyolefins, as most plastics that occur in the environment as a consequence of plastic pollution, undergo weathering and break up into very small particles, called microplastics. Because they are mostly not biodegradable, they accumulate and persist in the environment. To reduce plastic pollution plastic waste should be properly recycled. Hydrocarbon polymers, such as PE and PP, may be melted and extruded into pellets for reuse. HDPE is one of the easiest plastic polymers to recycle. As it is used in a wide number of industrial applications, postindustrial HDPE is an important source of HDPE that is collected and recycled. First, collected plastic is sorted and cleaned, to remove contaminants. HDPE is separated from other plastic fractions by sink-float separation. However, HDPE has a similar specific density to PP, and both float on the water bath, can be separated by using near-infrared (NIR) radiation techniques, unless the plastic is too dark and absorbs the infrared waves [53]. HDPE is then shredded reprocess by melting and turned into pellets of recycled HDPE (rHDPE), which can be used in manufacturing of rope, containers, cradles, toys, piping, recycling bin, trash cans, etc.

Properties of HDPE are commonly enhanced with colorants, additives, and fillers, which could have negative effect on the recycling of HDPE [54]. Non-HDPE packaging features should either be economically removed from the HDPE in the typical recycling process or be compatible with HDPE in future uses. Mineral fillers increase the density of HDPE, resulting in the failed separation in float-sink tanks. Additives designed to degrade the polymer in the primary use should be removed in recycling process not to shorten the useful life of the product made from the rHDPE. Optical brighteners are detrimental to recycling [54]. Barrier layers, coatings, and additives should be separable in the recycling process or be compatible with the HDPE, not to compromise quality of rHDPE [54].

HDPE is nonbiodegradable so it is imperative to recycle it. Also, it is more cost efficient to produce a product from rHDPE than from the virgin polymer. HDPE is produced using considerable amounts of fossil fuels and it takes a total of 1.75 kg of oil to manufacture 1 kg of HDPE [53].

The main problems in the recycling of PP arise from the easy degradability of this polymer both during its lifetime (mainly by photooxidation) and during processing and recycling operations [55]. Also, the presence of dyes, pigments, and additives influences recycling and limits the value of recycled PP (rPP) product [15,56]. It is currently not as economically viable to recycle PP, as it is to recycle other polymers, in particular HDPE, LDPE, and PET [57]. In the future, the difficultly and expense of the recycling process needs to be reduced, too. One of the problems is efficient sorting of plastics. The separation of PP from other plastic fractions is mainly done by sink-float separation. Polymers can be further separated using their melt flow index. If possible, the PP should also be sorted by color prior to processing [56].

PP is eventually affected by thermal degradation. According to some studies PP can be recycled in a “closed loop” four times before the thermal degradation has a negative impact on the polymer, while HDPE can be recycled 10 times [58]. Most of the rPP is mixed with virgin polymer in a ratio of around 1:3 to produce new item [57]. Nextek Ltd. (UK) has invented an innovative process to decontaminate food grade PP for reuse in a closed loop back into food packaging. The first phase involves melting PP at nearly 250°C to get rid of contaminants. The second step includes removing residual molecules under vacuum and solidification at about 140°C. The products made following this process can be blended with virgin PP at a rate up to 50% [59]. A main benefit of recycling PP is the reduction in the consumption of raw, finite resources, such as oil and propene gas. Also, there is up an 88% reduction in energy usage if plastic is produced from recycled plastic. PP can be recycled back into many different products, including: clothing and industrial fibers, food containers, dishware, speed humps, gardening apparatus (compost bins, garden edging, and plant pots) [57].

14.2.1.7 3D printing

At semicrystalline polymers like PE or PP, crystallization starts as soon as the temperature drops below the melt point, influencing the flow of extruded filament. Contraction stresses build up during cooling, resulting in huge

TABLE 14.3 Print settings for HDPE and PP.

	HDPE	**PP**
Print temperature (°C)	230–260	220–250
Bed temperature (°C)	70	85–100
Print speed (mm/s)	5	30 is ideal; up to 60-80
Bed adhesion	PP sheet, foam-core board	PP sheet, double-sided adhesive tape
Cooling fan		Required
Enclosure		Required

Adapted from Refs. [62,63].

warping stresses, making HDPE and PP challenging to 3D print [60]. HDPE is gaining on popularity because it is recyclable and can be easily transformed into a new material through recycling.

HDPE is one of the best impact resistance thermoplastics and has good machinability. As well as being very strong, HDPE is hard and opaque with moderate thermal stability. HDPE has a melting temperature at around 120°C and the processing window is from 230 to 260°C. The melt flow rate and extruding temperature of HDPE are similar to PLA [61]. Print settings for HDPE and PP [62,63] are given in Table 14.3. HDPE can be dissolved in limonene, which makes it ideal for 3D printing support material, and enables its application as a filler material for geometrically complex objects [62,64]. Because of low density and resistance to water absorption it can be 3D printed into objects that retain their buoyancy even at large sizes, for example, boats, or smaller objects that float, as pool or bath toys. It is great for drink accessories like coasters and koozies, food containers, and lids [62].

PP is great for high-cycle, low strength applications due to its fatigue resistance, semiflexible, and lightweight characteristics. It is ideal for low strength applications like living hinges, straps, leashes, etc. [63]. PP has a much better ability to elongate without breaking when compared to PLA filament and also resists impact better than PLA [65]. PP has a larger tendency to bend compared to PLA and it can resist deformation better under a load. Other advantages are better hinging capabilities, better chemical resistances, and a good surface finish [66].

Besides heavy warping another issue associated with PP is poor bed adhesion. The low surface energy of PP makes it extremely difficult to get good bed adhesion even with heated beds. Good adhesion is possible only with PP. Too good adhesion makes difficult to separate the printed part from the bed surface. The base layer can be protected with rafts, which act as an interface between the hot build surface and the bottom of 3D print. Trapping the heat around the 3D print will help eliminate warping [63]. Printing the first layer with 10°C higher temperature and turning off the heated bed after first layer reduces the warping.

The main advantages and disadvantages of HDPE and PP are summarized in Table 14.4. Also, some tips for 3D printing are given. In Fig. 14.2 PP 3D-printed object is shown.

FIGURE 14.2 3D-printed object from PP. *Image credits: Ultimaker B.V.*

TABLE 14.4 Advantages and disadvantages of HDPE and PP.

	HDPE
PROS	• Lightweight yet strong • Watertight • FDA approved • Recyclable
CONS	• Easy warping • Poor self-adhesion • Shrinkage
TIPS	• High nozzle temperature between 230 and 260°C, to flow consistently through the extruder. At too high temperature, the material starts to put out a toxic smell. • Heated print bed helps overcome self-adhesion and shrinkage issues when cooled, by keeping material stable and warm enough to keep its shape.
	PP
PROS	• Good impact and fatigue resistance • Better strength to weight ratio • Good heat resistance • Good chemical resistance • Smooth surface finish • Low density • Excellent flexibility
CONS	• Heavy warping • Low strength • Difficult to adhere to bed and other adhesives
TIPS	• Warping can be reduced with a stable temperature of the printing chamber, combined with a heated bed and high extruding temperature. • Printing at slightly higher temperatures (in the range of 240°C) can help with adhesion between layers. • A lower temperature for the first few layers prevents the part from fusing to the build surface. • Printing slowly can avoid jams. • PP has difficulty in adhering to the bed; additional adhesion is recommended.

Adapted from Refs. [62,63,66].

In Table 14.5 typical properties of 3D-printed filament (Ultimaker PP) are given. Applications for 3D-printed PP are beside functional prototypes versatile, such as living hinges, connectors, lab equipment, moldings, stationery folders, packaging, storage boxes, protective covers, and light shades. It is nonsuitable for long-term UV and/or moisture immersion, and applications where the printed part is exposed to temperatures higher than 105°C [67].

14.2.2 Poly(methyl methacrylate)

14.2.2.1 Development

Poly(methyl methacrylate) (PMMA) is one of the amorphous polymers that belong to the acrylate family. PMMA was discovered in the early 1930s by Rowland Hill and John Crawford at Imperial Chemical Industries (GB), followed by its first application by Otto Rohm, and brought to market in 1933 by Röhm and Haas AG (DE) [68]. The first major application of the polymer took place during World War II, when it was used for manufacturing the aircraft windows and bubble canopies for gun turrets [69].

14.2.2.2 Chemical structure and synthesis

PMMA is made from methyl methacrylate (MMA), a colorless liquid, the methyl ester of methacrylic acid. The chemical formula of PMMA is $(C_5O_2H_8)_n$. The IUPAC name is poly(methyl 2-methylpropenoate) or poly(methyl) methacrylate, and the structure-based name is poly[1-(methoxy-carbonyl)-1-methylethane-1,2-diyl]. Molecular weight of repeat unit as shown in Fig. 14.3 is 100.121 g/mol [70].

TABLE 14.5 Properties of 3D printing PP filament.

	PP
Density (g/cm^3)	0.89
Melt flow rate (MFR) (g/10 min)	20
Tensile strength: Yield (MPa)	8.7
Tensile strength: Break (MPa)	12.8
Tensile elongation: Yield (%)	18
Tensile elongation: Break (%)	300–716
Tensile modulus (MPa)	220
Flexural strength (MPa)	13
Flexural modulus (MPa)	305
Charpy notched impact strength (kJ/m^2)	10
Notched izod impact (kJ/m^2)	27
Durometer hardness	45 (Shore D)
Vicat softening temperature (°C)	115
Melting temperature (°C)	130
Volume resistivity (Ohm•cm)	$>10^{16}$
Gloss (%)	90
Haze (%)	28

Adapted from Ref. [67].

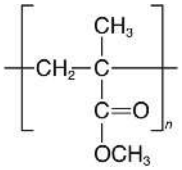


FIGURE 14.3 Repeat unit of PMMA.

PMMA can be obtained from its monomer using different polymerization mechanisms.

The monomer undergoes polymerization using the free radical and anionic initiations by bulk, solution, suspension, and emulsion techniques [71]. The most common technique is the free radical polymerization of MMA that can be performed homogeneously, by bulk or solution polymerization, or heterogeneously, by suspension or emulsion polymerization [72].

Radicals can be generated with radiation, heat, or chemical agents. The polymerization of MMA is most commonly started by initiators that decompose into radicals upon thermal or photochemical activation. After radical adds to a monomer, next generated radical undergoes chain propagation, ending with termination reactions [73]. With the free radical polymerization only limited control over the molecular weight, dispersity, and end groups of polymers formed is possible. Control of these properties enables living polymerization techniques, that is, anionic polymerization, group transfer polymerization, controlled radical polymerization, or stereospecific polymerization leading to more complex polymer architecture and polyacrylate polymers with different properties for specialized applications [73].

Bulk polymerization of MMA is the predominant method for producing amorphous PMMA used for manufacturing high-quality acrylic glass and other injection molded and extruded products. PMMA produced by solution polymerization of MMA is used to produce adhesives, paint resins, and additives. PMMA beads, which can then be molded, are produced by suspension polymerization. PMMA in resins, coating agents, processing agents, binders, and additives is made by emulsion polymerization of MMA

[72,74]. Polymerization in bulk or in solution proceeds in a series of continuous-flow stirred-tank reactors. For continuous bulk polymerization, reaction temperatures between 130 and 170°C are applied and the conversion range is between 40% and 80% [73]. Suspension polymerization is used to make molding powders wherein the reaction occurs between tiny monomer droplets suspended in a solution of catalyst and water. Grains of polymer are formed that have a strictly controlled molecular weight suitable for extrusion or molding [75].

14.2.2.3 Characteristics

The bulky pendent groups in the polymer structure prevent closely packaging and cause PMMA to be amorphous and nearly eliminate slip between polymer chains. This causes PMMA to be rigid, brittle, have a high Tg, and little mold shrinkage [69,76]. Mechanical strength of PMMA is compared to other plastics medium high, and the heat resistance is not good enough, as the use temperature is only 80°C [77].

The chemical properties of acrylic make possible to be completely transparent while remaining hard and highly resistant to scratching and impact. Typical PMMA grades allow 92% of light to pass through it, which is more than glass or other plastics. Some other advantages of acrylic plastic include certain chemical resistance, nontoxic composition, and dimensional stability, due to low moisture and water absorbing capacity [78]. Prolonged exposure to moisture or even total immersion in water has little effect on the mechanical or optical properties of acrylics. PMMA is resistant to oils, alkanes, and (diluted) acids and stays unaffected by aqueous solutions of most laboratory chemicals, by detergents, cleaners, but is not resistant to many (polar) solvents such as alcohols, organic acids, esters, and ketones [79,80].

PMMA shows quite small variation under the effect of UV-radiation and is known to withstand temperatures as high as 100°C [69]. Most commercial acrylic polymers are UV stabilized to improve the resistance to prolonged exposure to sunlight and give PMMA high resistance to UV light and weathering [81].

It is a lightweight material, which offers a high strength-to-weight ratio and is easily machined and processed by standard mechanical and thermal techniques. PMMA has good surface hardness, is able to be processed to a very high gloss finish, and offers a large number of color choices with excellent stability and surface effects.

Typical properties of generic PMMA polymer are presented in Table 14.6.

Acrylics are readily available and are inexpensive. It is a good alternative to PC when material strength is not a decision factor [82]. PMMA and PC are often used as a lightweight alternative to glass. PMMA is less likely to scratch and does not yellow over a period of time and has better cost-effectiveness compared to PC. Also, it has very high transmissivity and better optical clarity [81]. Compared to PS and PE the environmental stability of PMMA is better and is recommended for most outdoor application [81]. PMMA lies between general purpose PS and ABS [83].

The deficiencies of PPMA are low impact strength and limited chemical resistance; it is prone to attack by organic solvents. It is also rather brittle, cracking under load is possible, it has low fatigue resistance and limited heat resistance (80°C), as well as poor wear and abrasion resistance [81]. It has very low elastic deformation before failure, i.e., goes straight to brittle fracture. Flow properties of PMMA make processing slow compared to other materials. Because of poor flow properties it is difficult to mold thin-walled products [84].

PMMA can be modified by incorporating different additives. These modifications are performed to improve specific properties of the polymer, for example, impact resistance, chemical resistance, light diffusion, UV light filtering, or optical effects [81].

14.2.2.4 Processing

PMMA is suitable for processing by injection molding, extrusion, extrusion blow molding, thermoforming, and casting. It offers ease of processing and quite good flow properties, allowing use in a wide range of molding processes, though poor hot-melt strength limits processing methods [86]. If molded with excessive moisture content PMMA can exhibit aesthetic defects such as streaks, splay, or splash marks. Drying prior processing is recommended. Moisture level of 0.05% is needed for low barrel temperatures, whereas for high barrel temperatures, moisture level down to 0.02% or less is needed [86]. High injection pressure and necessity to inject slowly is recommended to get the correct flow. This is particularly important for optical moldings where visible weld lines will form if the correct parameters are not used. For thick moldings a high follow-up pressure is needed for a time period of 2–3 min. Internal stresses can be eliminated by heating at 80°C [84].

Extrusion is the second widely used processing technology for PMMA molding compounds. They are available in extruded and/or cast material in sheet, rod, and tube forms as well as custom profiles [79].

TABLE 14.6 Typical properties of generic PPMA polymer.

	PMMA
Density (g/cm^3)	1.08–1.1
Melt flow rate (MFR) (g/10 min)	10–30
Water absorption: 23°C, 50% RH (%)	0.3
Water absorption: 24 h, immersed (%)	0.1–0.4
Tensile strength: Yield (MPa)	41.6–55.4
Tensile strength: Break (MPa)	32–48
Tensile elongation: Yield (%)	3–4
Tensile elongation: Break (%)	5–21
Tensile modulus (GPa)	1.88–2.63
Flexural strength (MPa)	69.6–71
Flexural modulus (GPa)	1.83–2.74
Charpy notched impact strength (kJ/m^2)	4.6–15.1
Notched izod impact (kJ/m^2)	10.7–14.1
Rockwell hardness	102–116
Deflection temperature under load: 0.45 MPa (°C)	81–92.2
Vicat softening temperature (°C)	86–105
Melting temperature (°C)	130–140
Thermal conductivity (W/mK)	0.562
Surface resistivity (Ohm)	10^{13}–1^{4}
Volume resistivity (Ohm•cm)	$>10^{17}$
Dielectric constant	3.3
Transmittance (%)	85.6–90.1
Haze (%)	1–3.4

Adapted from Refs. [79,85].

Recommended processing conditions for extrusion according to Refs. [81,87] are:

- predrying: 4 h at 80°C,
- melt temperature: 180–250°C; 210–240°C,
- cylinder temperature: 190–230°C,
- screw design (L/D ratio): 20–30.

PMMA can be welded by all the plastics welding processes such as hot-blade, hot-gas, ultrasonic, or spin welding. Due to its transparency and stiffness, PMMA is also used as 3D printing material [81]. Several machining operations can be applied to PMMA. Acrylics are easily sawed, drilled, milled, engraved, and finished. Cut surfaces may be readily sanded and polished. They are also readily bend or thermoformed at low temperature and solvent bonding of properly fitting parts produces a strong, invisible joint [79].

14.2.2.5 Applications

PMMA polymer exhibits glasslike qualities: clarity, brilliance, transparency, translucence, and this at half the weight and with up to 10 times the impact resistance of glass. It is also more robust and has less risk of damage [81]. These unique properties enable PMMA to be used for store fixtures and displays, lenses and lighting fixtures, light pipes, LCD screens, and medical devices. Because of its clarity it is also often used for windows, tanks and enclosures around exhibits [82]. PMMA has excellent scratch resistance and very high gloss finish.

These properties, combined with PMMA's dimensional stability, enable its use in many different applications where lasting beautiful appearances are important, such as on furniture or kitchen or bath walls or cabinet facades [88].

Because it is inherently stable to UV-light, PMMA is used for many outdoor applications, in which it maintains its original color and finishes for many years [88]. Applications in architecture and construction reach from glass roofing, facade design, window and door profiles, canopies, panels to greenhouses, and aquariums. Other use is in automotive and transportation, signs and displays, and lighting. PMMA is also used in medical, density, and health care, due to its biocompatibility and because it is a high purity and easy-to-clean material [73,81]. Recently, it is used in 3D printing.

14.2.2.6 Recycling

Acrylic plastic is not recycled easily. It belongs to Group 7 plastic and is mostly not collected for recycling. Nevertheless, PMMA can be recycled in several ways, mostly subjecting the resin to pyrolysis. The raw materials used to manufacture MMA can be recycled and reused. When heated in appropriate conditions, PMMA splits back into its original monomer, MMA. Depolymerization is used industrially to recycle PMMA and to produce MMA which can be used again. The MMA recycled from PMMA has very high levels of purity. PMMA has been successfully depolymerized by contacting with molten lead resulting in MMA with a purity more than 98% [89]. PMMA can also be reground, melted, and extruded into new products. The recycled material can be used again [90]. Recycled PMMA sheets are used in different applications in construction, medical, public goods, lighting, advertisement sector, transport (cars, trains, and other vehicles), doors, and windows [89].

14.2.2.7 3D printing

PMMA is strong material, tough, and durable, that can withstand higher temperatures. It's also extremely rigid with very little flexibility. 3D-printed object can sustain a certain amount of stress without bending or deforming. Its high impact strength means that printed object will not as likely break if dropped or handled roughly [91]. PMMA provides wonderful light diffusion and the translucency/transparency of PMMA results in excellent clarity of printed object. When printed at higher temperature and slower printing speeds, 30 mm/s or less, it creates very translucent object [92].

Recommended 3D printing conditions according to Refs. [92,93] are:

- print temperature: 245−250°C; 230°C (−5°C/+10°C),
- bed temperature: 100°C; 100°C (−10°C/+5°C),
- print speed: 30−40 mm/s; 30−50 mm/s,
- bed adhesion: polyimide (PI) tape (also known as Kapton tape), blue painter's tape with glue (also known as Painter's tape, which is composed of acrylic adhesive and crepe paper backing), buildtak with glue,
- cooling fan: 10%−20%,
- enclosure: closed build chamber.

3D printing at lower temperatures leads to inconsistent flow and can produce bubbling and unevenness in the print line. These inconsistencies reduce the clarity of the material, turning it from transparent to translucent or even opaque [91]. A bed temperature of around 100°C is optimal to prevent warping. During cooling some shrinkage can occur. Good regulation of cooling speed is needed [91]. Some tips for 3D printing are given in Table 14.7.

PMMA responds very well to postprint finishing, such as sanding, drilling, or engraving. This ability, combined with its good solubility in acetone, enables smoothing and results in excellent finish quality [92]. It can be used in the process of lost wax casting, due to its ability to burn away cleanly without residue [94].

The main advantages and disadvantages of PMMA and some printing tips are summarized in Table 14.7.

PMMA is comparable in density to PLA and in hardness to ABS. Its tensile strength is almost twice the strength of ABS and PLA. It also has a maximum compression strength of 117 MPa which is much higher than compression strength of ABS [92]. PMMA compared to PC is easier to print, but is slightly less resistant [93]. It has slightly lower impact, heat and chemical resistance than PC, but it maintains high tensile strength, flexural strength, polishability, and UV tolerance [95].

In Table 14.8 typical properties of 3D printing filament are given, and in Fig. 14.4 PMMA print made by ZMorph VX Multitool 3D Printer is shown.

TABLE 14.7 Advantages and disadvantages of PMMA.

	PMMA
PROS	• Transmittance • Surface hardness • Excellent scratch resistance • UV stability
CONS	• Relatively low strength and poor impact resistance • Limited heat resistance (80°C) • Limited chemical resistance • Poor wear and abrasion resistance • Cracking under load possible
TIPS	• At lower printing temperatures the flow can be inconsistent with blobbing occurring. • Heated printing bed and enclosed chamber can prevent warping. • Slower printing speeds, 30 mm/s or less is recommended for better clarity.

Adapted from Refs. [81,91].

TABLE 14.8 Properties of 3D printing PMMA filament.

	PMMA
Density (g/cm^3)	1.17–1.18
Melt flow index (g/10 min)	13
Water absorption (%)	0.4
Tensile strength: Break (MPa)	52
Flexural modulus (GPa)	3.3
Notched izod impact (kJ/m^2)	11
Deflection temperature under load: 0.45 MPa (°C)	95–100
Vicat softening temperature (°C)	103–108
Melting temperature (°C)	220

Adapted from Refs. [96,97].

FIGURE 14.4 ZMorph VX Multitool 3D Printer and printed object from PMMA. *Image credits: ZMorph S.A.*

14.2.3 Polystyrene

14.2.3.1 Development

Polystyrene (PS) is commodity thermoplastic polymer, made from styrene. High-impact polystyrene (HIPS) is graft copolymer, made by the polybutadiene (PBD) copolymerizing with the styrene monomer. Styrene was obtained by Bonastre in 1831 and PS by Eduard Simon in 1839 as distilled oily substance from the storax, the resin of the American sweetgum [16]. Practical uses of PS were considered by Kronstein (1902) and Matthews (1911), and the polymerization reaction was studied by Ostromislenskii and by Staudinger (1929–1935) [98]. The company I. G. Farben began manufacturing PS in Ludwigshafen, in 1931. Since the 1930s styrene has been used in copolymers [99]. Large-scale commercial development began in 1935. In 1949 HIPS was introduced as a commercial plastic [100,101]. A process for producing HIPS was discovered by Charles F. Fryling in 1961. The composition was described as a PS matrix which contains uniformly dispersed particles of a graft copolymer of styrene and rubber. The graft copolymer consists of backbone chains of rubber to which are grafted side chains of PS [102].

14.2.3.2 Chemical structure and synthesis

PS is synthetic aromatic hydrocarbon polymer made from the monomer styrene, a derivative from benzene, obtained by the dehydrogenation of ethylbenzene. Styrene is the precursor to PS and several other copolymers. The source-based IUPAC name of PS is poly(ethenylbenzene) or poly(vinylbenzene), and the structure-based name is poly(1-phenylethane-1,2-diyl) [22]. It contains carbon and hydrogen and the chemical formula is $(C_8H_8)_n$. Molecular weight of monomer is 104.15 g/mol.

HIPS consists of the PS backbone with polybutadiene (PBD) chains branching from it in each direction [102]. Molecular formula is $(C_4H_6)_m$ $(C_8H_8)_n$; the repeat unit is shown in Fig. 14.5.

PS is formed by a chain-growth polymerization. Polymerization can be initiated by heat or free radicals (peroxides); it could be also cationic and anionic polymerization, or radiation polymerization [103,104]. The most common method is free radical polymerization using benzoyl peroxide as initiator. However, other initiators such as redox systems and azo compounds can be used as well. After initiation, a peroxy (benzoyl) radical combines with a styrene monomer, forming an active center. Until termination, the chain continues to grow one styrene monomer at a time. The relative stereochemical relationship of consecutive phenyl groups determines the tacticity [103].

Commercial PS is synthesized by bulk, suspension, or solution polymerization of styrene. The bulk or mass polymerization is completed in a two-stage polymerization process. In the first stage, the styrene is prepolymerized; in the second stage the mixture of dispersed polymer in monomer is then transferred to a tubular reactor. The pure molten PS that emerges from the extruder as filament is then cut into pellets [103]. The PS produced by mass polymerization is a fully transparent, atactic, low cost thermoplastic known as general purpose PS (GPPS) or crystal-clear PS. The other two processes, solution and suspension polymerization, can be carried out in batch or continuously. In the solution polymerization styrene is dissolved in solvent, such as ethylbenzene. The presence of solvent reduces the molecular weight and lowers the transparency of PS. In suspension process the monomer is suspended in droplets that are coated with some suspension agents, such as poly(vinyl alcohol) (PVA). Following polymerization, unreacted monomer is removed by steam distillation and the polymer is washed and dried [105].

HIPS is a heterophasic polymer build from a continuous PS phase and a disperse PBD phase. In order to produce the graft polymer, PBD is dissolved in styrene and polymerized. This reaction allows for two simultaneous polymerizations, that of styrene to PS and that of the graft polymerization of styrene-rubber [102]. HIPS is synthesized from a PBD/styrene solution by means of radical polymerization of styrene by bulk, or bulk-suspension method [106]. PBD is dissolved in styrene and with the added chemicals fed to the mixing section. The mass reaction occurs in the presence of solvent. The mixture is fed into reactors where polymerization takes place. At the end of reaction section the polymer solution is sent to a devolatilization section; the monomer and low-boiling compounds are removed from the polymer, which is sent to the pelletizing unit [107]. The rubber particles are chemically grafted or bonded to the PS matrix [108].

14.2.3.3 Characteristics

GPPS is an amorphous, clear, colorless commodity thermoplastic [109]. It is rigid, relatively hard, and rather brittle polymer. At temperatures below Tg, PS has medium to high tensile strength (35–55 MPa), but low impact strength (15–20 J/m) [103].

PS has good electrical properties, low dielectric loss, and is a very good electrical insulator. It has excellent optical clarity due to the lack of crystallinity, and is naturally transparent, though it can be colored with colorants [109]. PS is moisture resistant, has good chemical resistance to diluted acids and bases, and has excellent resistance to gamma radiation. Among other advantages, PS also has good dimensional stability and low shrinkage. It can also be radiation sterilized [103,109]. It has a rather poor barrier to oxygen and water vapor and dissolves in organic solvents,

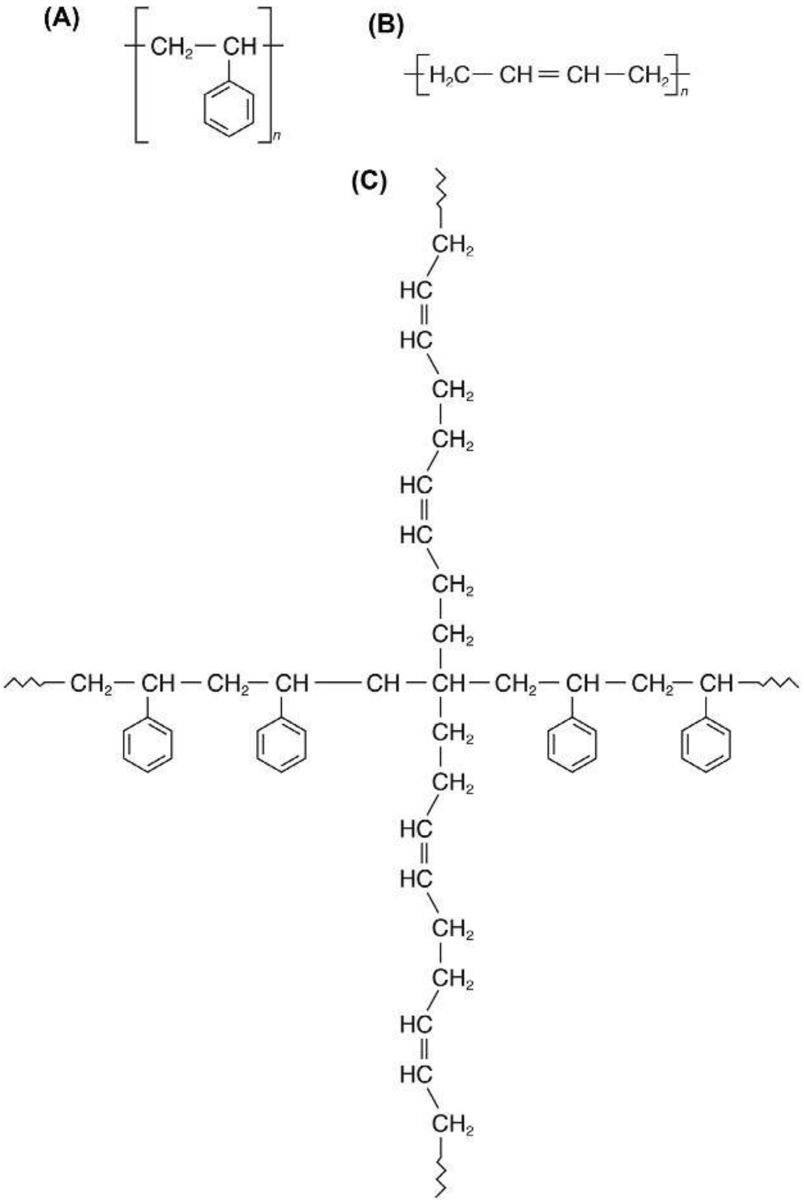


FIGURE 14.5 Repeat units of: (A) PS, (B) PBD, and (C) part of HIPS polymer structure.

hydrocarbons. PS has poor chemical and UV resistance and is flammable. It gets degraded on exposure to sunlight, due to photooxidation, which affects its mechanical properties [109,110]. It also has a relatively low melting point and poor thermal stability [111]. Its upper temperature limit for continual use is rather low due to the lack of crystallinity and its low Tg (100°C) [103].

PS has poor impact strength due to the stiffness of the polymer backbone. HIPS is impact-modified polymer made with the incorporation of soft PBD domains into glassy PS. The addition of rubber increases the toughness, and makes polymer incredibly durable, with a much higher impact resistance [111]. The stiffness and impact resistance of impact grades is determined by the amount of PBD present, which can be up to 15% by weight [112]. Though grafting gives a material with much higher impact strength, other properties, such as tensile strength, stiffness, hardness, and Vicat softening point, are not improved in the same way [108]. It is also water resistant, with low water absorbency.

HIPS is opaque and glossy, and can be easily painted, thanks to its amorphous structure [110]. It can be printed, glued, bonded, and decorated easily [113]. The advantages of HIPS are also its good dimensional stability and excellent machinability, and it is easily processable. It can be produced as FDA compliant. It's also very cost-efficient [114].

Typical properties of generic PS and HIPS polymers are presented in Table 14.9.

TABLE 14.9 Typical properties of generic HIPS and PS polymers.

	HIPS	PS
Density (g/cm^3)	1.04–1.06	1.04–1.05
Melt flow rate (MFR) (g/10 min)	2.3–8.2	0.8–11
Water absorption: 23°C, 50% RH (%)	0.098–0.1	0.098–0.11
Water absorption: 24 h, immersed (%)	0.1	0.1
Tensile strength: Yield (MPa)	16–30.5	18.4–56.3
Tensile strength: Break (MPa)	16–30.3	20–55
Tensile elongation: Yield (%)	1.5–2.1	1.4–2.1
Tensile elongation: Break (%)	24–70	1–3.9
Tensile modulus (GPa)	1.65–2.41	1.98–3.3
Flexural strength (MPa)	31–45.4	37.8–108.9
Flexural modulus (GPa)	1.37–2.45	1.86–3.51
Charpy notched impact strength (kJ/m^2)	4.83–11.1	1.89–10.1
Notched izod impact (kJ/m^2)	5.88–11.6	1.74–9.25
Rockwell hardness	54–106	70–105
Coefficient of friction	0.5	0.5
Deflection temperature under load: 0.45 MPa (°C)	83.9–88.9	76.7–86.1
Vicat softening temperature (°C)	81.7–100.6	81.1–106.1
Thermal conductivity (W/mK)	0.158–0.173	0.158–0.173
Surface resistivity (Ohm)	$1\cdot10^{9}$–$1.5\cdot10^{15}$	20–$1.5\cdot10^{15}$
Volume resistivity (Ohm•cm)	10^{12}–10^{18}	10^{2}–10^{18}
Dielectric constant	2.5	2.5
Gloss (%)	20–100	
Transmittance (%)	35–57	89–95
Haze (%)		0.3–1.07

Adapted from Refs. [115,116].

14.2.3.4 *Processing*

PS is a rigid, transparent thermoplastic, which is in a solid (glassy) state at room temperature. When heated above its Tg (100°C), PS starts to flow and can easily be extruded, injection molded, or compression molded. It becomes solid (rigid) again when it cools off. This temperature behavior is used for casting it into molds with fine detail [110]. PS can be also processed using vacuum forming or in the form of heat-expandable beads containing a suitable blowing agent which results in foamed PS products [111].

Besides PO family of plastics, HIPS is one of the most popular materials for thermoforming. Similar to PET, HIPS is brittle, amorphous, impact resistant, and clear, though with the addition of colorants its color can be changed to obtain the desired aesthetics [117]. HIPS also exhibits excellent malleability and because of its high tensile strength, it can be used in a wide range of applications. It also can be remolded several times. The good moldable properties mean that HIPS can be shaped into any form required using extrusion and injection molding processes [114].

HIPS flows more easily than PS. The extrusion grades of HIPS have melt flow rate (MFR) values between 2 and 10 g/10 min [108].

Recommended processing conditions for extrusion according to Ref. [108] are:

- predrying: no drying is required,
- melt temperature: 180–220°C,
- compression ratio: 3:1,
- screw design (L/D ratio): 24–30.

14.2.3.5 *Applications*

PS is one of the most popular commodity amorphous thermoplastic resins. It enables a lot of benefits that are highly valued by consumers, such as strength, durability, comfort, and safety [118]. Injection molded applications are used in household goods, containers, furniture, housings, and packaging [119]. Its neutral taste and odor are particularly important when it comes to food packaging applications.

Some of the most familiar uses of PS, according to Ref. [118], include:

- solid and film PS, used in rigid foodservice containers, CD cases, appliance housings, envelope windows, and many other products,
- PS foam, used in foodservice products and building insulation,
- composite products, used in tub and shower enclosures, automobile body panels, wind turbine parts, boats, and many other applications.

HIPS is a low cost material that is easy to fabricate and often used for low strength structural applications when impact resistance, machinability, and low cost are required. Due to its advantageous physical properties (strength and durability) it is used in food industry, automotive industry, and for manufacturing of various consumer products. Its major applications include covers, shelves, thermoformed machine housing and parts, automotive parts, general household appliances, housewares, toys, enclosures, machined prototypes, and model making. It is ideal for homewares such as shelving, electronic audiovisual equipment and housings, sports pitch surrounds, and general protective purposes [109,114].

Applications in packaging include food packaging (dairy packaging, meat trays, egg cartons, fruit and vegetable trays, hot and cold drinking cups), consumer packaging (cassettes and CD shell and covers, jewel box, etc.), industrial packaging (small foamed shapes), etc. HIPS's excellent hygienic qualities make it suitable for sensitive food packages and sterile medical device trays, Petri dishes, canisters, etc. [117,120].

Thanks to its strength and durability, HIPS is used for marketing purposes, for Point of Sale displays, handling trays, and promotional signage [114]. HIPS is used in graphic arts applications, such as promotional signs, display materials, garden stakes and tags, posters, and retail packaging, as well as 3D lenticular or moving images [113]. In 3D printing it is mostly used as support material.

14.2.3.6 *Recycling*

Recovery of PS via composting or biodegradation is not possible, that's why a cradle-to-grave approach should be adopted. PS can be mechanically recycled into several applications or chemically recycled to regenerate monomers or other small molecules. It can also be used in thermal recycling. The heat of combustion of PS polymers is approx. 41 MJ/kg, which is comparable to the value for oil [121]. When it is burned in municipal incinerators, PS yields carbon dioxide, water vapor, and ash [122]. The simplest and most common method of recycling PS is material recycling by mechanical compaction [123]. Recycling does not seem to have a significant effect on properties such as Tg or impact resistance of HIPS, while its malleability decreases significantly [124].

PS is 100% recyclable and comes back to life in items like picture frames, coat hangers, office supplies, construction products, and more, using less energy to produce these new materials.

14.2.3.7 *3D printing*

HIPS filament is a lightweight and durable thermoplastic which offers an alternative to PLA and ABS. HIPS is easy to print as PLA and is tough durable material, similar to the ABS [125]. It is ideal for printing in conjunction with ABS because it has a similar strength and stiffness as ABS. They are printed at around the same temperature. Though HIPS is as easy to print as ABS, it is much less likely to warp [126].

Recommended 3D printing conditions according to Refs. [125,127] are:

- print temperature: 210–260°C; 250°C,
- bed temperature: 90–110°C; 95°C,
- print speed: 40–100 mm/s; 50 mm/s,
- bed adhesion: glue-stick, vinyl hairspray, PI tape.

Printability of HIPS is good and has good adherence to the plate. It enables quick printing, without drawbacks as blocking of the nozzles during printing. HIPS is known for easy posttreatment, secondary operations like finishing (filing, sanding), soldering, and bonding and visual quality. Printed objects show excellent quality of parts, surface

TABLE 14.10 Advantages and disadvantages of HIPS.

	HIPS
PROS	• Good impact resistance • Transparency • Easy finishing • Low cost • Excellent soluble support material
CONS	• Brittle • Poor thermal stability • Poor solvent resistance • Subject to stress and environmental cracking • Highly susceptible to warping
TIPS	• The heating needs to be controlled quite strict, to prevent warping as the hot material is placed on the cooling layer. • Printed object must be cooled completely before removing it from the printing plate; it can bend if material is still warm. • When using HIPS as a soluble support material, printed object must be immersed in limonene at least 24 h. • ABS slurry on print bed surface can improve bed adhesion. • If the nozzle temperature is too low, the HIPS filament wont liquefy properly and will cause under-extrusion. • Printing at relatively low speeds (<40 mm/s) is needed for prints with lot of details. • Cooling fan must be at low speed or even turned off, to prevent deformations and warping.

Adapted from Refs. [109,120,128–131].

finishing and resolution, good dimensional stability, and precision of printed parts [125]. In Table 14.10 advantages and disadvantages of HIPS and some tips for printing are presented.

HIPS is an excellent soluble support material. It can be easily removed by submerging the object in limonene, which gives a slightly lemonlike smell to the finished product [128]. HIPS makes excellent support for the overhanging material and prevents the warping, deformation and collapse that would occur without the support [129].

HIPS also makes an excellent printing material. Its density is comparable to density of ABS but is less than density of other thermoplastics such as PLA, PETG, or PMMA. In mechanical properties, i.e., tensile strength, stiffness, and hardness, HIPS is similar to ABS, but is more easily soluble and can be machined, sanded, glued, and painted [129]. HIPS has high hardness and is highly shock-resistant, even in cold temperatures. It has comparable elastic deformation to other polymers used in FDM for a filament which is hard to break [125]. Typical properties of HIPS and PS filaments are given in Table 14.11.

TABLE 14.11 Properties of 3D printing HIPS and PS filaments.

	HIPS	PS (30% recycled)
Density (g/cm^3)	1.05	1.015
Melt flow index (g/10 min)	8.6	5.7
Water absorption (%)	<0.1	
Tensile strength (MPa)	26	19.5
Elongation at break (%)	40	18.1
Tensile modulus (GPa)	2	1.7
Flexural strength (MPa)	40	32.6
Flexural modulus (GPa)	2.1	1.52
Charpy impact strength (kJ/m^2)	130	7.5
Deflection temperature under load: 0.45 MPa (°C)	89	
Vicat softening temperature (°C)	88.5	
Melting temperature (°C)		240

Adapted from Refs. [132,133].

14.2.4 Poly(vinyl alcohol)

14.2.4.1 Development

PVA (PVOH) is vinyl polymer prepared from polyvinyl acetate (PVAc) that belongs to group of commodity polymers. Vinyl acetate monomer was first synthesized and patented of by Fritz Klatte (Germany) in 1912 [134]. He discovered that the catalyzed reaction of acetylene with acetic acid gave a readily polymerized low boiling liquid (vinyl acetate). PVA was first prepared by Hermann and Haehnel in 1924 by the saponification of PVAc, i.e., by the hydrolyzing PVAc in ethanol with potassium hydroxide [135]. The hydrolysis of polymerized vinyl esters to obtain PVA polymer was patented in the United States in 1939 [136]. Company Kuraray (Japan) was the first company in the world that began producing PVA (KURARAY POVAL) for commercial use in 1958 [137].

14.2.4.2 Chemical structure and synthesis

PVA is prepared from PVAc by replacement of the acetate groups with hydroxyl groups. It is a linear polymer which forms copolymers of vinyl alcohol and vinyl acetate. The chemical formula is $(C_2H_4O)_n$; molecular weight of repeat unit, shown in Fig 14.6B, is 44.05 g/mol [138]. IUPAC name of PVA is poly(vinyl alcohol) and the structure-based name is poly(1-hydroxyethane-1,2-diyl) [22].

While other vinyl polymers are prepared by polymerization of corresponding monomer units, PVA is prepared from another polymer, by either partial or complete hydrolysis of PVAc to remove acetate groups. The structure of commercial PVA is a copolymer of vinyl alcohol and vinyl acetate. PVAc is prepared by the free radical polymerization of vinyl acetate monomer. By dissolving PVAc in an alcohol and treating it with an alkaline catalyst hydrolysis or "alcoholysis" takes place [139]. The acetate groups are hydrolyzed by ester interchange with methanol in the presence of anhydrous sodium methylate or aqueous sodium hydroxide [135]. In this reaction the acetate groups from the PVAc are replaced with hydroxy groups without disrupting their long-chain structure [139].

PVA is composed mainly of 1,3-diol linkages [$-CH_2-CH(OH)-CH_2-CH(OH)-$], though a few percent of 1,2-diols [$-CH_2-CH(OH)-CH(OH)-CH_2-$] occur, depending on the conditions for the polymerization of the vinyl ester precursor [140]. The properties of PVA depend on the degree of polymerization and the degree of hydrolysis, specifically whether it is fully (1−2 mol% acetate groups) or partially hydrolyzed (up to 15 mol% acetate groups) [141]. Often PVA is classified into four classes: super, fully, intermediate, and partially hydrolyzed [142]. Repeat unit of partly and fully hydrolyzed PVA is shown in Fig. 14.6.

Polymerization reactions can be carried out in batch or in continuous process [143]. The hydrolysis of PVAc to PVA is carried out on a large industrial scale preferably by continuous so-called belt process. The solid PVA is formed from the solution, through gel state on the belt. At the end of the belt, the solid PVA is fed to a mill, comminuted, washed, and dried [144].

14.2.4.3 Characteristics

PVA has excellent film forming, emulsifying, and adhesive properties. It is odorless, tasteless, translucent, white to cream-colored, and nontoxic. Unlike other synthetic polymers, PVA is soluble in water. It is slightly soluble in ethanol, but insoluble in other organic solvents, and is resistant to mineral, animal, and vegetable oils and greases. PVA has high tensile strength, flexibility, as well as high oxygen and aroma barrier [135,145,146]. At PVA high tensile strength is combined with ease of film formation. Additionally, PVA resins show excellent adhesive and bonding characteristics [147]. However, mechanical properties are dependent on humidity. With higher humidity more water is absorbed, which lowers the tensile strength, but increases its elongation and tear strength is obtained. PVA is close to incompressible. The Poisson's ratio is between 0.42 and 0.48 [148].

The increase in molecular weight and %hydrolysis leads to increase in viscosity, tensile strength, water and solvent resistance, adhesive strength, and adhesion to hydrophilic surfaces. Decrease in molecular weight and %

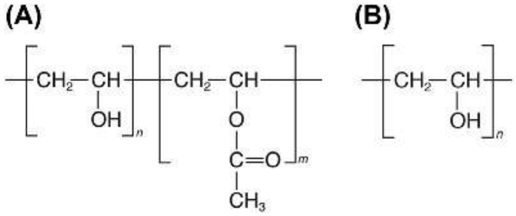


FIGURE 14.6 Structural formula of PVA: (A) partially hydrolyzed, (B) fully hydrolyzed.

TABLE 14.12 Typical properties of generic PVA polymer.

	PVA
Density (g/cm^3)	1.29
Tensile strength of film: break (MPa)	24.5–59.7
Tensile elongation of film: break (%)	90–650
Elmendorf tear strength (g)	100–1400
Melting temperature (°C)	180–230
Thermal conductivity (W/mK)	2

Adapted from Ref. [152].

hydrolysis leads to increase in solubility, flexibility, water sensitivity, and adhesion to hydrophobic surfaces [147]. Thermal stability of PVA: gradual discoloration about 100°C; darkens rapidly above 150°C; rapid decomposition above 200°C.

PVA filament has a translucent, white appearance. It has high tensile strength and flexibility and excellent adhesive properties [149]. PVA fibers have high tenacity, high Young's modulus, low elongation, low creep, and excellent resistance to severe weather (UV) and chemicals (alkali, acid, oil, etc.) [150]. PVA film has an excellent gas barrier to oxygen, nitrogen, hydrogen, but has a high moisture permeability. It has an excellent fragrance preservation of the contents and can keep products moisture and fresh as well. Because of hydroxyl groups in molecule, PVA is uncharged and shows good antistatic properties. Besides good tension and tearing strength its flexing resistance is 10 times to other films. Because of the strong polarity, PVA has the excellent printability. It has excellent weathering resistance and service life is very long [151]. Some properties of generic PVA polymer are presented in Table 14.12.

14.2.4.4 Processing

Most PVA films are cast from solution, whereas filaments are produced by solution wet spinning process. PVA meets the requirements of thermoplastic processing and can be processed using standard thermoplastic technologies, such as blown film extrusion, injection molding, and 3D printing. Its high mechanical strength and elasticity, excellent thermal shrinkage, caliber stability during stuffing, high thermal resistance, and aroma barrier make it suitable for food casings [153].

Thermal processing of PVA is challenging because its melting point is very close to its decomposition temperature. A melting point of PVA for sheet extrusion and blow molding is from 185 to 210°C with around a 2.2°C window of melt temperature before it degrades, turning yellow and cross-linking, which reduces water solubility [154]. Melt temperature during extrusion should not exceed 225°C. For production of blown films the temperature is between 195 and 205°C. Commercial standard extruders as known for the processing of thermoplastic polyolefins can be used [155].

Water-soluble injection molded shapes serve various fields of application like packaging, delivering, processing, and as mounting or assembly aid. One advantage in comparison to other polymers is the low shrinkage during the cooling phase [153].

Processing conditions for extrusion, according to Ref. [155], are:

- predrying: no drying is required,
- melt temperature: 195–215°C,
- compression ratio: 3:1,
- screw design (L/D ratio): 25.

14.2.4.5 Applications

PVA has varying roles in commercial and industrial applications such as papermaking, textiles, and printing [156]. It is used in sizing agents in production of textile yarns and paper-based products, or as paper adhesive in spiral tube winding and solid board production, or in paper coating. It is also employed as a component of adhesives and emulsifiers, as a water-soluble protective film, and as a starting material for the preparation of other resins or fibers (polyvinyl nitrate, carbon fibers (CFs)) [139].

Major applications of PVA fibers and filaments include geo-textiles, ropes, agriculture and fish nets, filters, and other nonwovens, as well as composites (fiber cement) [150].

Recently, PVA is used in injection molding of soluble containers for active release of detergents and agrichemicals and in 3D printing as support structure material. It is utilized for various industrial applications to enhance the mechanical properties of films because of its compatible structure and hydrophilic properties [157]. It is used in flexible packaging, in laminated films, and as a water-soluble film or as barrier layer in rigid packaging. Other applications are backing sheet in hygiene and incontinence products, film used in the water transfer printing process, a release liner or form release. PVA fibers and films are used in medicine and pharmacology because of their ability to swell, absorb toxic products, decompose necrotic masses, and reduce blood loss [158].

14.2.4.6 Recycling

The water soluble film is a green environmental product. PVA is nontoxic and does not restrain from the growth of microorganism. It also degrades completely. PVA film will be decomposed into water and carbon dioxide. Solubility is between 15 and 90°C, and is related to PVA film thickness and temperature. PVA films are environment-friendly and they do not release toxic gasses upon incineration. The overall market for water-soluble applications is expected to expand at a CAGR of 4.9% from 2017 to 2025 [159].

PVA is a biodegradable polymer, and its degradability is enhanced through hydrolysis because of the presence of hydroxyl groups on the carbon atoms. Moreover, it is water-soluble and has a hydrophilic nature. Rates and environmental conditions for degradation may vary; these conditions include composting in the presence of oxygen, underneath soil layers, in aqueous environment [160].

14.2.4.7 3D printing

PVA is used as support material for multi-extrusion 3D printing (Fig. 14.7). It is ideal when printing complex geometries that require supports for large overhangs, deep internal cavities, detailed features on models, and intricate geometries [161]. It has good adhesion to PLA, PA, and copolyester (CPE). The biggest advantage of PVA filament is its ability to dissolve in water and is biodegradable with no hazardous by-products [161,162].

Recommendations for PVA 3D printing according to Refs. [163,164] are:

- print temperature: 200–210°C; 185–200°C,
- bed temperature: optional, when used 50–70°C; 45–60°C,
- print speed: under 25 mm/s,
- bed adhesion: polyetherimide (PEI) tape or adhesive spray,
- cooling fan: high or medium setting.

Advantages and disadvantages of PVA and some tips for 3D printing are summarized in Table 14.13. In Table 14.14 some of typical properties of 3D printing filament are shown.

PVA is a flexible filament, which can have influence on printing. At too low nozzle temperature it does not liquefy properly and causes under-extrusion and it can easily bend under high stress [163]. A greater chance of clogging

FIGURE 14.7 3D-printed object from PVA. *Image credits: Ultimaker B.V.*

TABLE 14.13 Advantages and disadvantages of PVA.

	PVA
PROS	• Great support material • Easily adheres to other polymers • Water soluble • Biodegradable and nontoxic • Fairly easy to print
CONS	• Partially hydrolyzes (breakdowns) at a temperature of 180°C • Moisture sensitive • It can release some unpleasant vapor if overheated • Expensive
TIPS	• Bending filament under high stress, resulting in the material not lying properly, can be prevented by lowering printing speed. • Drying filament exposed to moisture in a hot air oven 6 h on 60–70°C will demoisturize PVA and prevent it from boiling when 3D printed. • Matterhackers's PVA does not require a heated bed. • Makerbot's filament requires limonene to dissolve it.

Adapted from Refs. [163,164].

TABLE 14.14 Properties of 3D printing PVA filament.

	PVA
Density (g/cm^3)	1.23–1.31
Melt flow index (g/10 min)	14–20
Tensile strength: Break (MPa)	78
Tensile elongation: Break (%)	9.9
Tensile modulus (GPa)	3.86
Charpy notched impact strength (kJ/m^2)	1.6
Vicat softening temperature (°C)	60
Melting temperature (°C)	163–200
Thermal conductivity (W/mK)	0.2

Adapted from Ref. [166].

exists if the nozzle is left hot when not extruding [164]. At fast printing, a lot of filament is pushed into the heating chamber; filament buckles under the stress and causes a clog within the nozzle [163].

PVA filament does not suffer much from warping during 3D printing; nevertheless cooling is recommended. Cooling during printing gives the best results because it prevents sagging and messy melts [163].

PVA requires more careful storage than HIPS. If PVA is exposed to air that contains too much water it will begin to lose its tensile strength and degrade. HIPS is easily stored, but requires a chemical solvent to remove. PVA dissolves away completely in water, leaving sharp, clean lines on the overhanging areas of the object [165].

14.3 Engineering polymers

14.3.1 Styrene terpolymers

14.3.1.1 Development

ABS is an important engineering thermoplastic polymer. It is a copolymer belonging to styrene terpolymer chemical family, made up of three monomers: acrylonitrile, butadiene, and styrene [167]. Styrene was first obtained by Bonastre in 1831 by distillation of storax balsam. Matthews in 1911 described the thermal and catalytic polymerization to yield a substance able to replace celluloid, glass, and hard rubber. Polymerization of styrene was further studied by Dufraise and Moreau in 1922, Ostromislenskii (1911–25), and Staudinger (1929–35) [98]. High-impact grades were produced since 1948 and isotactic PS was obtained by Natta in 1955 [16]. Since the 1930s styrene has been used in copolymers with elastomeric characteristics. Today it is used for manufacturing important copolymers and terpolymers such as styrene–acrylonitrile (SAN), styrene–divinyl benzene (S-DVB), styrene–maleic anhydride, acrylonitrile–butadiene–styrene (ABS), and others [16].

SAN copolymer has been available since the 1940s and while its increased toughness over styrene made it suitable for many applications, its limitations led to the introduction of a rubber (butadiene) as a third monomer in terpolymer [168]. In attempts to produce bulletproof plastic sheets in 1945 polymer systems were developed from special butadiene acrylonitrile (BAN) copolymers and SAN copolymers with high molecular masses. The first patent that claimed a product made of a mixture of BAN elastomer and SAN copolymer was issued in 1948. Improvements in polyblending technology and the development of grafting processes during the 1950s led to a significant improvement of ABS terpolymer properties [16]. ABS was introduced to commercial markets by the Borg-Warner Corporation in 1954.

Acrylonitrile styrene acrylate (ASA) is a terpolymer composed of the monomers acrylonitrile, styrene, and acrylate. ASA was first introduced by BASF in about 1970 as Luran S. The intent was to create a material similar to ABS but with better weather resistance [169].

14.3.1.2 Chemical structure and synthesis

The atomic components building ABS are carbon, nitrogen, and hydrogen, with carbon being the predominant atomic species. The IUPAC name is buta-1,3-diene; prop-2-enenitrile; styrene. Monomer molecular weight of acrylonitrile is 53.06 g/mol. Monomer molecular weight of 1,3-butadiene is 54.09 g/mol, and the monomer molecular weight of styrene is 104.15 g/mol. Molecular formula and molecular weight of ABS repeat unit, shown in Fig. 14.8, are $(C_{15}H_{17}N)_n$ and 211.31 g/mol. It is named as copoly(acrylonitrile-butadiene-styrene) or poly(acrylonitrile-co-butadiene-co-styrene) [22,170,171].

In ASA, the oxygen is also present in chemical structure, besides carbon, nitrogen, and hydrogen. It is named acrylonitrile-styrene-acrylate copolymer or poly(acrylonitrile-stat-styrene-stat-acrylate). The chemical formula and molecular weight of ASA repeat unit are $(C_{18}H_{23}NO_2)_n$, MW = 285.39 g/mol [172].

Acrylates contain vinyl groups directly attached to the carbonyl carbon, and are prepared by treating acrylic acid with the corresponding alcohol in presence of a catalyst. The backbone of the ABS is formed from phenylene (styrene) and buta-1,3-diene. Acrylonitrile forms a grafted side chain onto the backbone with bonding nitrile on the butadiene unit [173]. Acrylonitrile is a synthetic monomer produced from propylene and ammonia, whereas butadiene is produced as a by-product of ethylene production from steam crackers and styrene is manufactured by dehydrogenation of ethylbenzene [167].

ABS polymers can be produced by two methods: by a mechanical blending of an SAN copolymer with a BAN rubber or by grafting of styrene and acrylonitrile onto polybutadiene (PBD). Styrene and acrylonitrile are being grafted onto rubber by chemical grafting, chemical grafting blending, or physical mixing. Chemical grafting blending is the most frequently used method [174].

Properties are determined by changing the blend ratio of components and their interactions. Monomer ratio varies from 15% to 50% for acrylonitrile, 5%–30% for butadiene, and 40%–60% for styrene, as well as SAN/PB ratio 90–40/10–60 [171]. The number and size distribution of PB rubber particles, thermoplastic, and rubbery phase characteristics as well as grafting degree and morphology determine the properties of ABS, as well [175,176]. Processability, heat resistance, surface hardness, and chemical resistance of ABS are controlled by content, molecular weight, and distribution of SAN. Styrene provides rigidity and ease of processability. Chemical

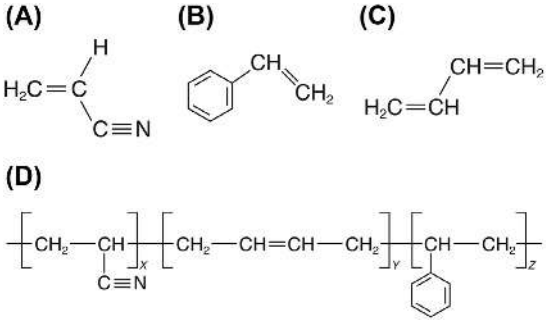


FIGURE 14.8 Monomers of: (A) acrylonitrile, (B) styrene, (C) butadiene, and (D) repeat unit of ABS.

resistance, rigidity, and heat stability are supplied by acrylonitrile, whereas toughness and impact strength are influenced by PB [176].

The first commercial production of ABS was carried out as a multistep emulsion batch reaction process, where first PB is prepared as a watery rubber into which styrene and acrylonitrile are introduced and copolymerized [177]. The emulsion process requires the use of several processing additives such as emulsifiers and salts, and there can be significant variability in the material from batch to batch. Impurities from the additives typically remain in the finished material in detectable levels, which contributes to the resin's yellowish tint [178]. A continuous mass polymerization of styrene and acrylonitrile in a rubber-styrene solution is made by dissolving PB in liquid acrylonitrile and styrene monomers and then polymerizing the monomers by the introduction of free-radical initiators. The mass polymerization uses only few process additives and yields a much more consistent, purer product with less color, compared to emulsion process. The emulsion process is more flexible and suited to the synthesis of specific materials, though it is a much more intensive technology in terms of raw materials, chemicals, and utility consumption [177,178].

ASA is an acrylic elastomer modified SAN copolymer. Terpolymer can be produced by either a patented, proprietary reaction process or by a graft process. ASA is formed by the distribution of an acrylic elastomer in the form of very fine particles during copolymerization of styrene and acrylonitrile. It is being bonded to the hardening component by grafted styrene-acrylonitrile chains [179,180]. Structure of ASA is core−shell structure with a cross-linking PB core and a grafted SAN copolymer shell. The base poly(butyl acrylate) elastomer is produced by polymerization of an acrylate in emulsion, and grafted with styrene and acrylonitrile (PSAN). The purpose of the PSAN shell is to anchor the elastomer particles in the PSAN matrix. The grafted elastomer is isolated by spray drying or by coagulation followed by drying [181].

14.3.1.3 *Characteristics*

ABS is a strong, stiff and durable, chemically resistant material. It is known for its strength, toughness, and resistance to distortion from heat and solvent cracking [182]. ABS shows excellent mechanical properties, high rigidity, good impact resistance (even at low temperatures), good abrasion and strain resistance, high dimensional stability, good weldability, good insulating properties, high surface brightness, and excellent surface aspect [183]. It has a very good resistance to diluted acid and alkalis, a moderate resistance to aliphatic hydrocarbons, but gets easily attacked by polar solvents (aromatic hydrocarbons, halogenated hydrocarbons, and alcohols). It is usually opaque, although some grades can now be transparent, and it can be given vivid colors [167,183]. ABS is versatile in the range of color and surface texture options that can be achieved and it can be manufactured to a very high-quality finish. It is lightweight and suitable for a vast range of applications [184].

ASA was developed as an alternative to ABS, as polymer with improved weather resistance. The outstanding weatherability of ASA is due to the acrylic ester elastomer [169]. ASA is structurally very similar to ABS. It has great toughness and rigidity, good chemical resistance and thermal stability, outstanding resistance to weather, aging and yellowing, and high gloss. Durability and superior impact resistance, even at low temperatures, easy coloration, and easy processability are other features of ASA [185,186]. ASA is resistant to saturated hydrocarbons, low-aromatic gasoline and lubricating oil, vegetable and animal oils, water, aqueous solutions of salts, and dilute acids and alkalis. However, it is attacked by concentrated inorganic acids, aromatic and chlorinated hydrocarbons, esters, ethers, ketones, and some alcohols [179]. Typical properties of generic ABS and ABA polymers are given in Table 14.15.

Shortcomings of ABS are poor weathering resistance and poor solvent resistance for aromatic ketones and esters. It has low dielectric strength, low continuous service temperature, and limited uses in association with food industry. ABS scratches easily and can suffer from stress cracking in the presence of some grease [167,188]. ASA has 10 times the weathering resistance and resistance to ultraviolet radiation of ABS, higher long-term heat resistance, and better chemical resistance. It is significantly more resistant to environmental stress cracking than ABS, especially to alcohols and many cleaning agents [189]. Higher stiffness, impact strength, and better weatherability properties are advantages of ASA compared to PP [181].

Disadvantages of ASA are similar to disadvantages of ABS. ASA melts with other thermoplastics such as PO, PS, and PA giving rise to moldings of poor strength. It generates toxic smoke when burned [185]. When processed, ASA forms weak weld lines and highly anisotropic properties [190]. ABS and ASA are relatively inexpensive polymers, though compared to PS and PE, they are more expensive.

14.3.1.4 *Processing*

ABS has a broad processing window and can be processed on most standard machinery. It can be injection molded, blow molded, or extruded. ASA resin can be processed by most conventional methods. It can be injection

TABLE 14.15 Typical properties of generic ABS and ASA polymers.

	ABS	ASA
Density (g/cm^3)	1.03–1.08	1.05–1.07
Melt flow rate (MFR) (g/10 min)	2.1–36	3–23
Water absorption: 23°C, 50% RH (%)	0.19–0.55	0.2–0.37
Water absorption: 24 h, immersed (%)	0.27–0.31	0.3–0.32
Tensile strength: Yield (MPa)	29–57	35–56
Tensile strength: Break (MPa)	15–50	29.3–51.4
Tensile elongation: Yield (%)	2–4.1	2.8–6
Tensile elongation: Break (%)	2–36	2–50
Tensile modulus (GPa)	1.5–3.14	1.78–2.58
Flexural strength (MPa)	53.9–86.2	55.3–80
Flexural modulus (GPa)	1.86–2.96	1.81–2.67
Charpy notched impact strength (kJ/m^2)	5.9–27.3	7.6–17.9
Notched izod impact (kJ/m^2)	8.8–25.2	6.3–20
Rockwell hardness	95–117	95–116
Coefficient of friction	0.11–0.46	
Deflection temperature under load: 0.45 MPa (°C)	77–104	87.8–106
Vicat softening temperature (°C)	89–108.3	90–109.4
Melting temperature (°C)	222–225	200
Thermal conductivity (W/mK)	0.173–0.202	0.173
Surface resistivity (Ohm)	$4 \cdot 10^3 – 5 \cdot 10^{15}$	$10^{12} – 10^{15}$
Volume resistivity (Ohm•cm)	$5.1 \cdot 10^3 – 2.5 \cdot 10^{16}$	$10^{12} – 10^{15}$
Dielectric constant	3.09–3.1	3.4–3.9
Gloss (%)	15–98	21–96.5
Transmittance (%)	83.7–93	85.5–90
Haze (%)	1.46–4.02	1–8

Adapted from Refs. [185,187].

TABLE 14.16 Processing conditions for extrusion of ABS and ASA.

	ABS	ASA
Predrying	3 h 70–80°C; up to 3.7 h 75–90.5°C	2.5–3.5 h 80–85°C
Melt temperature (°C)	196–225.5; 200–245	230
Compression ratio	2.75:1	1:2–1:4
Screw design (L/D ratio)	25–30	25–30

Adapted from Refs. [167,178,185,192,193].

molded, structural foam molded, and extrusion-blow molded, as well as extruded. Extruded sheet can be thermoformed [179]. Recoverable shear strain, shear stress, and coefficient of friction in injection molding of ASA are the key factors controlling the formation of surface defects, such as “chevrons,” nonuniform haze, and step defect [191]. Processing conditions for extrusion of ABS and ASA are given in Table 14.16.

14.3.1.5 *Applications*

Several properties like high impact strength, heat performance, and good balance between toughness/strength/temperature resistance coupled with its ease of processing and high-quality surface finish enable ABS a very wide range of applications. ABS is suitable for use in automotive and transportation industries, domestic appliances, telephone handsets, computer, and other office equipment housings, medical/health-care applications, building and construction, safety helmets, pipes, fittings, engineering parts, etc. It can prove a cost-effective, attractive, and top-performing thermoplastic with a wide variety of benefits and uses [167,184]. ABS is one of the mostly used 3D printing filaments.

ASA imparts excellent resistance to discoloration, embrittlement and degradation from UV sunlight, atmospheric oxygen, and heat from processing compared to ABS. Because of these attributes, ASA is an ideal material for automotive industry as well as several other outdoor applications which required long-term performance [186]. Thanks to its excellent retention of physical properties and appearances in outdoor applications for a long time, it is used as a material for automobile exterior, outdoor appliances, sporting goods, general purpose housings, motorcycle parts, construction and furniture finishing sheet, etc. [194]. It is also used in building/construction and as telecommunications components [179].

14.3.1.6 *Recycling*

ABS and ASA plastics are recyclable, but not every recycling company has the equipment yet to sort and chip ABS or ASA. Used parts consisting solely of ABS or ASA can be recycled, after cleaning and size reduction, to give new moldings.

The resin identification codes list ABS and ASA in group 7, together with SAN, PC, PA, PEI, PU, and others. Unfortunately, these mixtures make these products undesirable for recycling. Mostly number 7 and codeless items go directly to the landfill [195]. The Standardization Administration of the People's Republic of China (SAC) has defined 140 material codes for different types of plastics: 9 for ABS and 13 for ASA [196]. Some of prosumer 3D printer users have adopted a voluntary recycling code based on the Chinese system because of the lack of similar code system in EU countries [5]. Recycle fraction in current supply is 3.8%–4.2%. At processing and recycling CO_2 footprint for ABS primary production is 3.6–4 kg/kg, CO_2 footprint for recycling is 2.5–3.1 kg/kg [197].

In Germany, Luran S (ASA) waste is classified under Waste Code No. 57 108 (polystyrene wastes), and does not require any special disposal measures. Luran S waste can be disposed of to landfill. It can be incinerated in a suitable incinerator. The fuel value of Luran S is about 10 kWh/kg, about 70% higher than that of dry wood. Complete combustion gives carbon dioxide, water, and nitrogen, the nitrogen being oxidized to a limited extent to give nitrogen oxides [192].

ABS/ASA products that are mostly collected for recycling are monitor/TV cases, cellphones, calculators, most computer plastic, Lego bricks, and most FDM 3D-printed parts that are not bioplastic such as PLA. Recycled resin, clean without any contamination, may be added up to 30% to the virgin resin in the manufacturing of moldings. This is possible because of high thermal stability of ASA [192]. At very high temperatures (400°C), the material decomposes into butadiene, acrylonitrile, and styrene, which can be harmful if incinerated.

14.3.1.7 *3D printing*

ABS is one of the most versatile materials available for 3D printing. Good processability and low melting temperature make ABS particularly suitable for processing by FDM 3D printing. The properties of the materials such as temperature and strength are of great importance on their performance in FDM [178]. ABS is tough, able to withstand high stress and temperature, and it is also moderately flexible. These properties make ABS a good general-purpose 3D printing filament, especially with items that are frequently handled, dropped, or heated [60].

ASA 3D printing material is a standard production-grade thermoplastic, like ABS. It is known for high-impact resistance, higher temperature resistance, and with many of the same printability drawbacks that are seen with ABS. Warping is still a consistent issue, as well as the potentially dangerous fumes, that the plastic emits during printing, due to the presence of styrene [198]. Cold ASA print will warp or split or have terrible layer adhesion; a hot print will have better layer adhesion, with some stringing and some rougher overhangs [199].

The settings for printing with ASA are very similar to those used for ABS, as seen from Table 14.17. This means printing at high temperatures, using heated bed (110°C is recommended) and good adhesion, but without using a cooling fan during printing. Printed part can be finished by controlled exposure to acetone via the process of "vapor smoothing" [200]. Unfinished ASA prints have very high sensitivity to temperature, rendering them prone to warping, cracking, and shrinkage under less than ideal conditions [201].

Both, ABS and ASA absorb moisture from the air and need to be dried before printing. Recommended temperature and time for drying for ABS are 65°C, 3 h, and for ASA 60°C and 4 h [202].

TABLE 14.17 Print settings for ABS and ASA.

	ABS	ASA
Print temperature (°C)	210–250; 220–240	220–245; 230–250
Bed temperature (°C)	80–110; 90–100	90–110, 90–100
Print speed (mm/s)	30–40; 40–80	35–70
Bed adhesion	PEI or PET tape, ABS slurry, hairspray, glue sticks	PEI or PET tape/sheet ABS/ASA slurry
Cooling fan	0%–50%	10%
Enclosure	Not required	Not required

Adapted from Refs. [60,65,198,203].

TABLE 14.18 Advantages and disadvantages of ABS and ASA.

	ABS
PROS	• Quite low cost • Good impact and wear resistance (high endurance to heat pressure and stress) • Less oozing and stringing (smoother finish) • Water resistance • Easily treated to obtain great finish
CONS	• Heavy curling and warping • Shrinking (dimensional inaccuracy) • Odor while printing • Susceptible to sunlight, UV radiation – not suitable for outdoor use
TIPS	• A large heater is needed to reach higher melting temperature. • Good ventilation is needed because of unpleasant smell and potentially dangerous vapors during printing. • With heated build plate, and enclosed, heated build chamber, ABS stays warm during printing, cools down slowly, resulting in less curl up. • High nozzle temperature (230°C) is better, but if stringing and oozing occur it has to be lowered (by 5°C). • If the filament doesn't stick, the parts aren't sturdy or the surfaces have a rough feel, increasing the temperature by 5°C is recommended. • If ABS filament "bubbles" and crackles, it is probably too wet. • At a dual extrusion print, PLA can be a good breakaway support material as it does not adhere strongly to ABS.
	ASA
PROS	• Good impact and wear resistance • High Tg • High UV resistance • Tough
CONS	• Very temperature sensitive, warps and splits if temperatures are not quite right determined and kept • Very energy-intensive printing process • Requires ventilation (release of noxious and toxic styrene gas during printing) • More expensive than ABS
TIPS	• Print temperature is generally 250°C; printing too hot is not so problematic as printing too cold. • A slurry of ABS or ASA and acetone gives an excellent film onto which printed layer can adhere. • To avoid cracking the printer's cooling fan should be turned down to 10% or just 5% power. • Vapor smoothing with acetone gives nice surface. • Adjusting nozzle distance by 0.02 mm at a time is recommended, until the right distance is found.

Adapted from Refs. [198,200,203–205].

Due to the higher temperature that is required for printing with ASA, the printed parts are frequently prone to overheating, which can create significant print quality issues. To minimize overheating, the bottom few layers of ASA should be printed with a higher extruder temperature, and a few layers later the temperature should be decreased by 5°C. Another option is to run the part cooling fan at a very low speed, typically in range of 10%–25% [198]. Tips for printing, together with advantages and disadvantages of ABS and ASA, are given in Table 14.18.

TABLE 14.19 Properties of 3D printing ABS and ASA filaments.

	ABS	ASA
Density (g/cm^3)	1.08	1.06
Melt flow index (g/10 min)	41	14.2
Water absorption: 23°C, 50% RH (%)	0.7	
Tensile strength: Yield (MPa)	39	29
Tensile strength: Break (MPa)	33.9	26.8
Tensile elongation: Yield (%)	3.5	2
Tensile elongation: Break (%)	4.8	3.5
Tensile modulus (GPa)	2.03	1.37
Flexural strength (MPa)	70.5	63.7
Flexural modulus (GPa)	2.07	2.59
Charpy notched impact strength (kJ/m^2)	22	45
Notched izod impact (kJ/m^2)	10.5	21.8
Deflection temperature under load: 0.45 MPa (°C)	99	98
Vicat softening temperature (°C)	105	103
Melting temperature (°C)	225–245	220–250
Thermal conductivity (W/mK)	0.173	
Surface resistivity (Ohm)		10^{13}
Volume resistivity (Ohm•cm)	10^{16}	10^{14}–10^{15}
Dielectric constant	3.2	2.97–3.04
Gloss (%)	90	

Adapted from Refs. [209–212].

In comparison to PLA filament, ABS is less brittle and more ductile. It is strong, ductile material with wear resistance and higher temperature resistance. ABS has more finishing techniques available: it sands easier than PLA and different methods for excellent postprocessing are available. Acetone is used to melt away the layer lines, and it can be postprocessed with acetone to provide a glossy finish [206].

ABS is used in a lot of applications, including concept models, functional prototypes, jigs and fixtures, manufacturing tooling, and occasionally in production parts, especially it is recommended in lightweight end-of-arm tools and other functional parts. Common 3D prints with ABS are interlocking parts like gears, parts exposed to heat like a car cup holder, or prototyping [65,207].

ASA produces the best aesthetics of any of FDM thermoplastic and with a surface-finish of extremely high quality [207]. Another benefit of ASA is its ability to retain both shape and color over time [201]. It is particularly suited to fit-form and functional prototypes and parts, especially for outdoor use. Its wide selection of colors and matte finish makes it ideal for attractive prototypes in consumer sporting goods, tools, and automotive components and accessories [208].

Typical properties of ABS and ASA 3D printing filament are given in Table 14.19. In Fig. 14.9 two 3D-printed ABS objects made by students at course 3D printing (Univeristy of Ljubljana, Faculty of Natural Sciences and Engineering (UL NTF)) are shown.

14.3.2 Polylactide

14.3.2.1 Development

Polylactic acid or polylactide (PLA) is aliphatic polyester derived from renewable resources, such as corn starch, cassava roots, tapioca, sugarcane, etc. Two main monomers are used for polymerization of PLA: lactic acid (2-

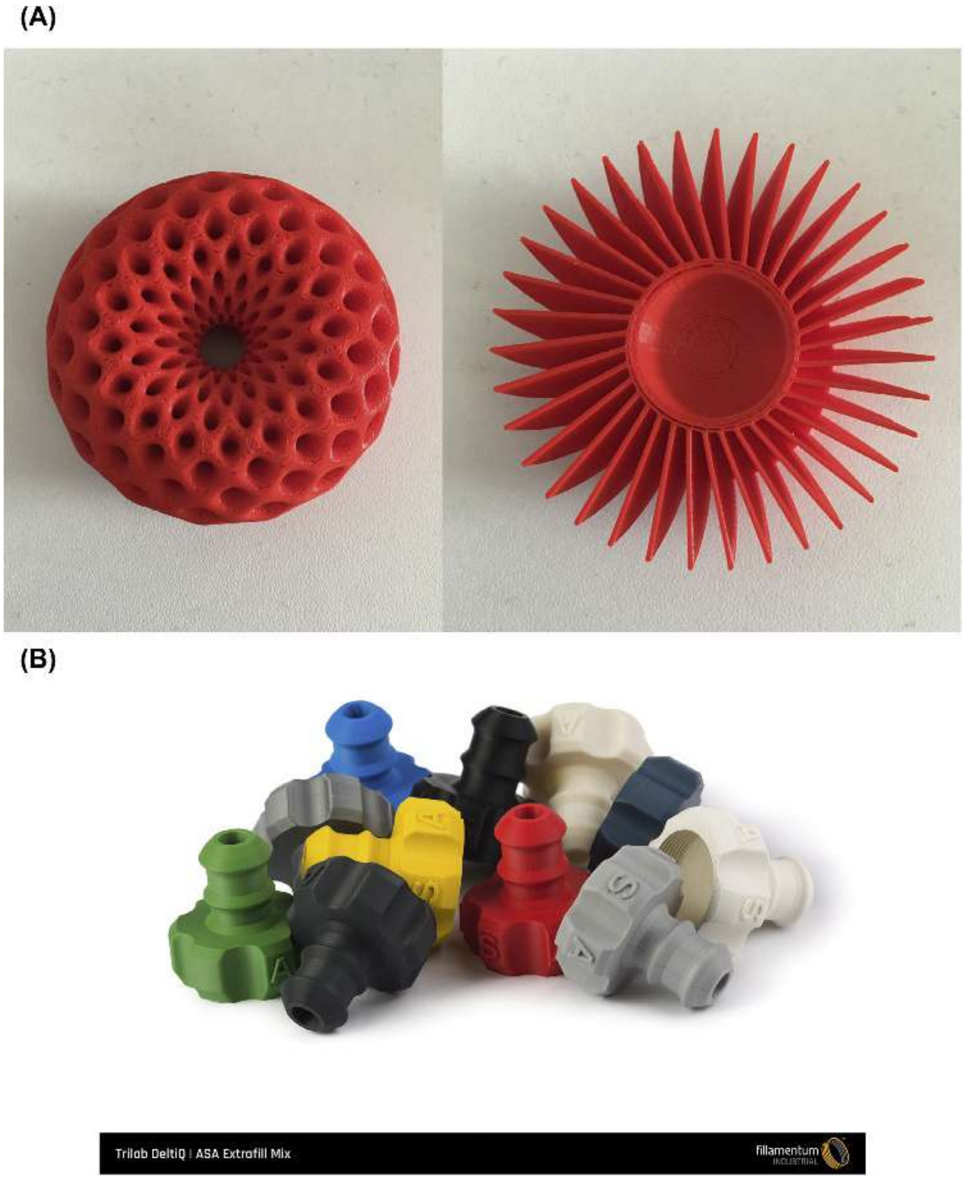


FIGURE 14.9 3D-printed objects from (A) ABS and (B) ASA. *(A) Image credits: UL NTF. (B) Image credits: Fillamentum Manufacturing Czech s.r.o.*

hydroxy propionic acid) and the cyclic di-ester, lactide [213]. Lactic acid was isolated for the first time by the Carl Wilhelm Scheele in 1780 from sour milk. In 1895, lactic acid started to be produced commercially by the German pharmacy Boehringer Ingelheim [214]. PLA was first synthesized in 1932 by Wallace Carothers (DuPont), by heating lactic acid under vacuum while removing the condensed water, which resulted in low-molecular-weight PLA. Technology was developed further by DuPont, with high molecular weight polymers obtained in 1955 [215]. A high-molecular-weight PLA was synthetized by ring-opening polymerization of the lactide. PLA was first used in combination with polyglycolic acid (PGA) as suture material in the United States in 1974 [216]. Resurgence of interest emerged in 1980s, and the commercial production in Blair, Nebraska, in 2001 [215].

14.3.2.2 Chemical structure and synthesis

The structure-based IUPAC name of PLA is poly(2-hydroxypropanoic acid), and the molecular formula and molecular weight of repeat unit, shown in Fig. 14.10, are $(C_6H_8O_4)_n$ and 72.06 g/mol [217,218].

Lactic acid is produced via fermentation or chemical synthesis. It is two optically active configurations; the L(+) and D(−) stereoisomers are produced by bacterial fermentation of carbohydrates [219]. Generally, pure L-lactic acid is used for PLA production [220].

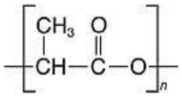


FIGURE 14.10 Repeat unit of PLA.

Lactide is a cyclic dimer formed by removing water under mild conditions and without solvent. PLA can be made from lactic acid by different polymerization processes: polycondensation, ring-opening polymerization and by direct methods, like azeotropic dehydration, and enzymatic polymerization [221]. None of the process is simple or easy to execute. PLA synthesis requires rigorous control of conditions (temperature, pressure, and pH), the use of catalysts, and long polymerization times [222]. Currently, direct polycondensation and ring opening polymerization are the most used production techniques [223]. The direct condensation polymerization is based on esterification of monomers (lactic acid) by the aid of some solvents whereby water is removed using progressive vacuum and high temperatures. It is the least expensive route, but is difficult to obtain high molecular weights [143]. Producing high-molecular-weight PLA polymers by azeotropic dehydrative condensation, where organic solvents are introduced into reaction mixture to ease up removal of water, is more practicable. Third industrially used process for high-molecular-weight PLA production is polymerization through formation of lactide monomer first, which is then converted by the help of the catalyst into final product. Ring-opening polymerization of lactide can be carried out in melt or solution by cationic, anionic, and coordination mechanisms, depending on the initiator utilized [216]. Currently, the biggest producer of PLA, NatureWorks (NB, US) produces PLA using specific solvent-free process where combination of melt polycondensation and ring-opening polymerization is utilized [224].

The quality of the monomers lactic acid and lactide as well as the chemical changes induced during polymerization and processing are crucial parameters for controlling the properties of the PLA products [225].

14.3.2.3 Characteristics

PLA can be produced as amorphous or semicrystalline, with up to 40% crystallinity. PLA resins contain more than 93% of L-lactic acid, though most PLAs are made up of L- and D,L-lactide copolymers [143]. Molecular structure, presence of ordered structures, molecular orientation, and crystallinity determine the properties of PLA. The molecular weight has a significant impact on the properties of polymers such as degradation, mechanical strength, and solubility [223]. High-molecular-weight PLA is a colorless, glossy, rigid thermoplastic material with properties similar to PE, PP, or PS [226]. Tg ranges from 50 to 80°C, Tm from 130 to 180°C. The mechanical properties of PLA vary from soft and elastic, to stiff and high strength, and can be obtained to satisfy different applications [143]. The basic mechanical properties of PLA are between those of PS and PET [227]. PLA has relatively high mechanical strength and high mechanical resistance, though it has a lower maximum continuous service temperature and is more brittle than PET [228]. Often plasticizers are added which improve its flexibility, tear resistance, and impact strength, as pure PLA is rather brittle [229]. By annealing, adding nucleating agents, chain extending, forming composites, and introducing cross link structures the mechanical properties of PLA polymers can be enhanced.

Optical properties of PLA are important in dyeing operations and where clarity is desirable property. PLA has very good optical properties in terms of transparency and gloss and also a good and smooth appearance [223]. PLA has good fat, oil, and flavor barrier properties [230]. Films made of PLA have very high moisture vapor transmission, and very low oxygen and CO_2 transmission rates. Intermediate vapor permeability level results in a breathability level that enables use in packaging for ready-to-eat vegetables [230].

PLA is not very resistant to chemicals; it has good chemical resistance to hydrocarbons, vegetable oils, and the like. A good solvent for PLA is chloroform, chlorinated or fluorinated organic compounds, and many other organic solvents. The surface energy of 49 mJ/m^2, with higher dispersive component, suggests a relatively hydrophobic structure compared to other biopolymers, with wetting tension, enabling easier printing [143,230]. Typical properties of generic PLA polymer are given in Table 14.20.

PLA when burning has low flammability and smoke formation and has low toxic level. Under typical use conditions, PLA is very stable and will retain physical properties for years. High-molecular-weight PLA is also naturally resistant to supporting bacterial and fungal growth, which allows it to be safely used for applications such as food packaging and sanitation [223].

The heat performance of PLA is typically between LDPE and HDPE and its impact strength is comparable to HIPS and PP whereas impact modified grades have much higher impact strength comparable to ABS [229]. PLA is known for rather low thermal stability and high sensitivity to hydrolytic degradation. This renders PLA suitability for high temperature applications such as containers made for holding hot liquids. Hydrolysis under high humidity

TABLE 14.20 Typical properties of generic PLA polymer.

	PLA
Density (g/cm^3)	1.24–1.25
Melt flow rate (MFR) (g/10 min)	2–20
Water absorption: 23°C, 50% RH (%)	0.12–0.46
Tensile strength: Yield (MPa)	15.5–71.7
Tensile strength: Break (MPa)	13.8–70.3
Tensile elongation: Yield (%)	9.8–10
Tensile elongation: Break (%)	1–12
Tensile modulus (GPa)	2.87–3.58
Flexural strength (MPa)	9–110.3
Flexural modulus (GPa)	0.31–9.51
Charpy notched impact strength (kJ/m^2)	1.4–5.5
Notched izod impact (kJ/m^2)	3.4–4
Coefficient of friction	0.38–0.45
Deflection temperature under load: 0.45 MPa (°C)	50–120
Vicat softening temperature (°C)	54.5–60.5
Melting temperature (°C)	154–171
Gloss (%)	90
Transmittance (%)	90
Haze (%)	2–85

Adapted from Refs. [231,232].

conditions leads to degradation of PLA. PLA is considered inferior to PET for long-term food storage applications due to higher permeability. PLA packaging material has been found to be more permeable to moisture and oxygen compared to other plastics. PLA is not recommended for applications where toughness and impact resistance are important characteristics of material [233].

14.3.2.4 Processing

Several processing technologies are used for large-scale production of PLA, including extrusion, injection molding, injection stretch blow molding, casting (film and sheet), extrusion blown film, thermoforming, foaming, fiber spinning, and electrospinning [223]. The rheological properties of PLA, especially the shear viscosity, have important effects on thermal processes, such as injection molding, extrusion, film blowing, sheet forming, fiber spinning, and thermoforming. PLA melts are shear thinning, similar to PS. The molecular weights and the amounts of plasticizer govern the useable melt viscosities required for melt processing [221].

The limiting factors for processing conditions for biopolymers are degradation at the upper limits of temperature and shear, and lack of homogeneity at the lower limits. The results of exceeding the upper limits are degradation of the polymer, resulting in molding defects such as weld lines, discoloration, or a strong odor in the final product [234]. The major problem is the limited thermal stability during the melt processing. PLA undergoes thermal degradation at temperatures above 200°C [143].

PLA is sensitive to the combination of moisture and temperature. Drying the polymer prior to use is recommended to protect the intrinsic properties of the material, especially its mechanical properties [230]. PLA is stable in the molten state, provided that the drying procedures are followed.

Recommended processing conditions for extrusion according to Refs. [235,236] are:

- predrying: 4–6 h at 85°C,
- melt temperature: 190–210°C,
- compression ratio: 2.5:1 to 3:1,
- screw design (L/D ratio): 24:1 to 32:1.

14.3.2.5 *Application*

PLA biodegradability, its optical, physical, and chemical properties make it an ideal choice for a number of applications in biomedical, textile, and packaging sector [228]. PLA is mainly used in the packaging industry for blow-molded bottles, injection-molded cups, bowls, thermoformed cups and trays, spoons, forks, and straws. Other applications include disposable bags and trash liners as well as compostable agriculture films. PLA is also an excellent choice for biomedical and pharmaceutical applications such as drug delivery systems and sutures because PLA is biodegradable, hydrolyzable, and generally recognized as safe [229]. In the form of fibers and nonwoven fabrics, PLA also has many potential uses, for example, as upholstery, disposable garments, awnings, feminine hygiene products, and diapers. Thanks to its biocompatibility and biodegradability, PLA has also found ample interest as a polymeric scaffold for drug delivery purposes. Because of good biodegradability, PLA is increasable used as medical implants in the form of anchors, screws, plates, pins, rods, and as a mesh [237]. PLA is besides ABS most common desktop printing material in FDM 3D printing.

14.3.2.6 *Recycling*

One of the major advantages of PLA is its biodegradability. Polymer degradation occurs mainly through scission of the main chains or side chains of macromolecules. PLA has a relatively long half-life of hydrolysis due to steric effects where the alkyl group hinders the attack by water [238]. The rate of this hydrolytic degradation is primarily temperature and humidity dependent [223]. PLA has a degradation half-life in the environment ranging from 6 months to 2 years, depending on the size and shape of the product, its isomer ratio, and the temperature [226].

PLA is largely resistant to attack by microorganisms in soil. The polymer must first be hydrolyzed at elevated temperatures (about 58°C) to reduce the molecular weight, before biodegradation can start [216]. The primary mechanism of degradation occurs by a two-step process starting also with hydrolysis, followed by bacterial attack on the fragmented residues [223]. PLA products rapidly degrade in both aerobic and anaerobic composting conditions [239]. Most commercial PLA films are 100% biodegradable and compostable. However, the biodegradation time can vary greatly depending on composition, crystallinity, and environmental conditions [229]. Under industrial composting conditions PLA will degrade into carbon dioxide and water in approximately 6 weeks [240].

PLA can be broken down to its original monomers by a thermal depolymerization process or by hydrolysis. The resulting monomer solution can be purified and used for subsequent PLA production without any loss of quality [233]. There are two methods for PLA chemical recycling: primarily hydrolysis or solvolysis to L-lactic acid or L-lactic acid−based compounds, and second process, depolymerization to the cyclic dimer, L-lactide. Both methods have problems with low yield of monomers in a short period and require the removal of catalysts [216].

Besides chemical recycling, some streams of PLA material can also be reprocessed through mechanical recycling. The major problem of mechanical recycling is the thermal stability of PLA. In the study of Pilin et al. [241] it was reported that only the tensile modulus remains constant at thermomechanical recycling, whereas rheological properties, tensile properties, and hardness decrease substantially after several cycles.

Sorting PLA in recycling facilities is difficult due to low volumes and in many cases, the PLA container looks like PET. Because of this, the possibility of mixing the different materials together is possible [216].

14.3.2.7 *3D printing*

PLA is one of two common plastics used on FDM printers. As PLA is so versatile, it is a great starting filament to use for the majority of 3D prints. It is popular material in 3D printing because the print temperature is lower compare to most other filaments and because it flows nicely, won't warp, and is not prone to stringing or blobbing. Print quality issues due to improper temperature include oozing, stringing, and under-extrusion. It is easy to sand, drill, or cut after printing. It can be pigmented easily, prints can be dyed, with acrylic based paints, oil or cellulose spray paints [242]. PLA 3D filament has low odor, higher print detail/resolution, excellent first layer adhesion, improved adhesion between layers, reduced warping, curling, and failed prints, making it a popular plastic for makers, prosumers, and schools [243,244].

Recommended 3D printing conditions according to Refs. [245,246] are:

- print temperature: 190−230°C; 200−220°C,
- bed temperature: none needed; 50−70°C,
- print speed: 40−80 mm/s,
- bed adhesion: PI tape, blue painter's tape, hairspray (or adhesive spray),
- cooling fan: 45%−100%.

TABLE 14.21 Advantages and disadvantages of PLA.

	PLA
PROS	• Biodegradable, environmentally friendly • Low cost • Low processing temperature • Less likely to warp, compared to other materials • Does not emit any unpleasant fumes during the printing process • Stiff and good strength • Good dimensional accuracy • Good shelf life
CONS	• Low heat resistance • Can ooze and may need cooling fans • Filament can get brittle and break • Not suitable for outdoors (sunlight exposure) • Prints degrade over time
TIPS	• The extruded filament needs to cool down below Tg as quickly as possible, to prevent stringing and producing other artifacts. Fan that cools the 3D printed part from all directions is highly recommended. • To avoid stringing reducing temperature by 5–10°C helps, and will help prevent the excess oozing. To avoid under-extrusion increasing the temperature by 10°C is recommended. • Printing at relatively low speeds (<40 mm/s) gives the best results, if print has a lot of details. • A heated bed is not required, only when printing large surfaces, a heated bed at 60–70°C gives the best result. • With the right temperature and cooling, it is possible to bridge long gap parts; no support raft needed. • Brittle or snapping filament is the consequence of absorbed moisture. Moisture causes, that printed layers get harder to bind together, and those that do bind together tend to be distorted.

Adapted from Refs. [245,247,248].

Advantages and disadvantages of PLA and some tips for printing are given in Table 14.21.

PLA is ideal for printing things like gadgets, toys, household items, and anything else that does not need too much flexibility. Since is biocompatible, it is safe for use with things that come into direct contact with the skin [249]. PLA is food safe material, used to make food containers, disposable tableware, and garbage bags. However, 3D printing in PLA will not create food safe containers because 3D printing can cause many tiny gaps and cavities in your prints that will harbor moisture and food residue [242].

The ease with which PLA melts allows for some interesting applications in 3D printing, so-called lost PLA casting. This is a process where PLA is printed in the shape of an interior cavity and then encased with plaster-like materials. The PLA is later burned out as it has a lower melting temperature than the surrounding material. The end result is a void that can be filled (often with molten metal) [250].

Because PLA flows better than ABS, it is possible to print more detailed objects with higher speeds [251]. It is especially good at producing sharp corners. ABS is a little more durable than PLA and slightly stronger and is often preferred due to its improved ductility over PLA [251,252]. PLA has shinier and smoother appearance. The amount of gloss depends on the vendor, color, and print temperature. PLA can deform because of heat and is less sturdy than ABS [251–253]. Typical properties of 3D printing filament are given in Table 14.22. PLA printed objects, model of castle Snežnik and model of small animals living in Postojna cave, printed at University of Ljubljana, Faculty of Natural Sciences and Engineering are shown in Fig. 14.11.

14.3.3 Polyamides

14.3.3.1 Development

The term nylon refers to a family of synthetic polymers called linear PAs. They belong to the group of engineering polymers. PAs are made from a dicarboxylic acid, molecule containing two carboxyl functional ($-$COOH) groups on each end, and a diamine, molecule containing amine functional ($-\mathrm{NH_2}$) groups on each end. The resulting PA is named on the basis of the number of carbon atoms separating the two acid groups and the two amines. PAs are made also from an amino acid that is able to undergo self-condensation, or its lactam, characterized by the functional group ($-$CONH$-$) in a ring [256].

PAs were developed in the 1930s. Around 1938 Schlack discovered PA 6, known as nylon 6, which was commercialized in 1939 [16]. Carothers started polycondensation studies in 1929 and obtained PA 66 as a fiber-forming

TABLE 14.22 Properties of 3D printing PLA filament.

	PLA
Density (g/cm^3)	1.24
Melt flow index (g/10 min)	6.1
Water absorption: 23°C, 50% RH (%)	<0.1
Tensile strength: Yield (MPa)	49.5
Tensile strength: Break (MPa)	45.6
Tensile elongation: Yield (%)	3.3
Tensile elongation: Break (%)	5.2
Tensile modulus (GPa)	2.35
Flexural strength (MPa)	103
Flexural modulus (GPa)	3.15
Charpy notched impact strength (kJ/m^2)	<5
Notched izod impact (kJ/m^2)	5.1
Deflection temperature under load: 0.45 MPa (°C)	55–65
Vicat softening temperature (°C)	55–85
Melting temperature (°C)	145–160
Thermal conductivity (W/mK)	0.13
Gloss (%)	90

Adapted from Refs. [254,255].

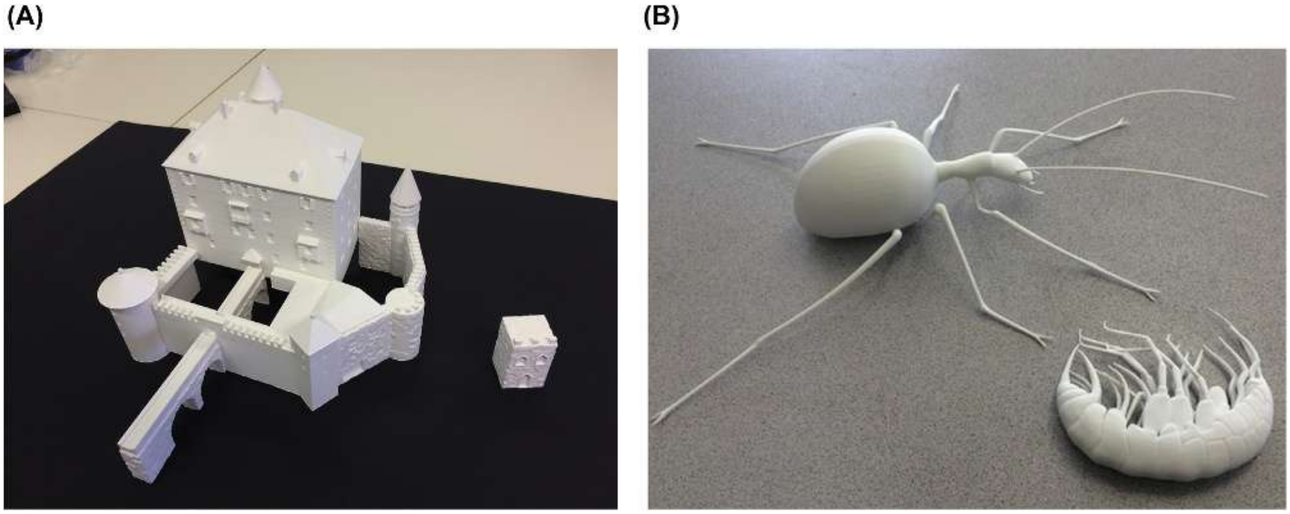


FIGURE 14.11 3D-printed objects from PLA: (A) model of castle Snežnik and (B) animals living in Postojna cave. *Image credits: UL NTF.*

polymer in 1935 [16]. In 1938, DuPont announced the invention of the first wholly synthetic fiber ever produced with the trade name Nylon [257]. The very first product was a toothbrush with nylon bristles. PA 66's first real success came with its use in women's stockings, in about 1940. During the World War II PA 66 was needed to make war materials, like parachutes and ropes [258].

Since then many different aliphatic or semiaromatic PAs were developed for use in textiles and different plastic products. PA 46 is commercially available since 1980s, and fills the gap between engineering polymers and high-performance polymers [259].

14.3.3.2 *Chemical structure and synthesis*

One of the most common PAs is PA 66 made from adipic acid and hexamethylenediamine, named poly(hexamethylene adipamide). The structure-based name is poly(iminoadipoyliminohexane-1,6-diyl). The chemical formula is $(C_{12}H_{22}N_2O_2)_n$ and molecular weight of repeat unit is 226.32 g/mol [260].

From caprolactam as a starting material, PA 6 is obtained. IUPAC name is poly(hexano-6-lactam) and the structure-based name is poly[imino(1-oxohexane-1,6-diyl)]. The chemical formula is $(C_6H_{11}NO)_n$ and molecular weight of repeat unit is 111.14 g/mol [261].

PA 12 is made from ω-aminolauric acid or laurolactam monomers, that each have 12 carbons. It is named poly(-dodecano-12-lactam). The structure-based name is poly(imino-1-oxododecamethylene). The chemical formula is $(C_{12}H_{23}NO)_n$ and molecular weight is 197.32 g/mol [262].

PA 46 is made from two monomers: one containing four carbon atoms, 1,4-diaminobutane (putrescine), and the other six carbon atoms, adipic acid. IUPAC name is poly(hexamethylene succinamide) or poly(tetramethylene adipamide) or poly[imino(1,6-dioxohexamethylene) iminotetramethylene]. The chemical formula is $(C_{10}H_{18}N_2O_2)_n$ and the molecular weight is 198.26 g/mol [263]. In Fig. 14.12 repeat units of mentioned PAs are shown.

PAs are made in a condensation reaction in a step-growth polymerization. They are formed by reacting difunctional monomers containing equal parts of amine and carboxylic acid, so that amides are formed at both ends of each monomer. The repeating unit consists of one of each monomer, so that they alternate in the chain, similar to the so-called ABAB structure of polyesters (PESs) and polyurethanes (PURs). Most PAs are made from the reaction of a dicarboxylic acid with a diamine. Another type of PA is formed from lactam or amino acid with itself. In the so-called AA structure the repeating unit corresponds to the single monomer [264−266].

PA 66 is synthesized by polycondensation of hexamethylenediamine and adipic acid, where equivalent amounts of both compounds are combined with water in a reactor. The first step is preparation of salt formed from mixture of precise stoichiometric quantities of the two monomers [267]. The concentrated salt solution, an ammonium/carboxylate mixture, together with a molecular weight stabilizer, is heated in a reactor. Removing water drives the reaction toward polymerization through the formation of amide bonds from the acid and amine functions. The polymerization process takes place either in batches or continuously [267]. Polymer can either be extruded and granulated or directly spun into fibers by extrusion through a spinneret and cooling to form filaments.

PA 6 is synthesized by ring-opening polymerization of caprolactam. First, caprolactam reacts with water, the amide bond in caprolactam breaks, and aminocaproic acid is produced. In the addition reaction a lactam unit joins the growing molecule at its amine end. Simultaneously, condensation reaction takes place, in which two growing molecules react to form an amide linkage at liberating a water molecule [268]. Main applications of the anionic polymerization of caprolactam are the reactive extrusion (REX) or the reaction injection molding (RIM) process.

PA 46 is obtained by a classical polycondensation of diamines (1,4-diaminobutane) and diacids (adipic acid) or amino acids. PA 12 can be produced with polycondensation of ω-aminolauric acid, a bifunctional monomer with one amine and one carboxylic acid group or with ring-opening polymerization of laurolactam. Ring-opening polymerization is the preferred route for commercial production [269].

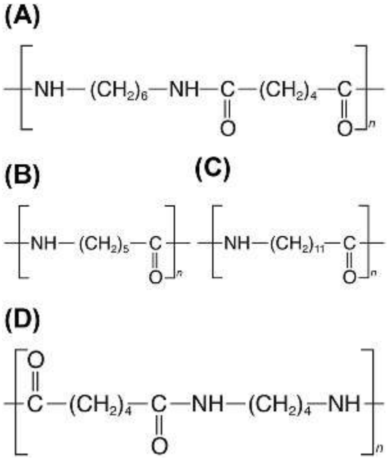


FIGURE 14.12 Repeat units of PAs: (A) PA 66, (B) PA 6, (C) PA 12, and (D) PA 46.

Through use of additives, fillers, pigments, plasticizers, modifiers, or processing aids, processability and properties can be altered. PAs can be modified using comonomers or stabilizers during polymerization to introduce new chain end or functional groups, which changes the reactivity and chemical properties [270].

14.3.3.3 Characteristics

PA is a popular material in the plastics industry, known for its toughness and flexibility [271]. PAs are semicrystalline materials, characterized by high degree of crystallinity, and are generally tough materials, possessing high tensile strength with good thermal and chemical resistance. By varying monomers, it is possible to make products that are hard and tough or soft and rubbery. They have good abrasion and wear resistance [256]. PA tends to absorb moisture from its surroundings, influencing dimensional stability of material. The impact resistance and flexibility of PA tends to increase with moisture content, while the strength and stiffness below the Tg decrease. They have good resistance to most chemicals, lubricants, oil products, and organic solvents; however, strong acids, alcohols, and alkalis can attack PA [256].

Although, they exhibit similar properties, slight differences do remain. PA 66 is distinguished in higher strength properties, high hardness and deformation stability, increased heat resistance, chemical, and climate resilience. It also shows good dynamic strength, cracking resistance, and resistance to cyclic loadings. It is capable to hold its shape constantly at temperature up to 180°C and temporary at 200°C [272].

PA 66 compared to PA 6 absorbs slightly less moisture, exhibits higher heat and wear resistance, and better insulating characteristics. PA 6 compared to PA 66 has better ductility, better creep and UV-resistance, higher impact resistance at low temperatures, and better surface appearance. Processability of PA 6 is better than PA 66, due to its lower viscosity. PA 6 is also slightly less expensive than PA 66 [273].

PA 12 has lower water absorptivity and lower impact resistance than other PAs, but shows good chemical resistance, resistance to abrasions, and displays good dimensional stability and reasonable electrical properties. It has outstanding impact strength, excellent resistance to stress cracking, and good fatigue resistance under high-frequency cyclical loading [274].

Key properties of PA 46 are good thermal performance and good mechanical properties, particularly at high temperatures. PA 46 exhibits the highest temperature resistance, with heat deflection temperature of 160°C at 1.8 MPa. Mechanical resistance of PA 46 is superior to PA 66; its fatigue resistance is 50 times that of PA 66. It has outstanding stiffness, fatigue and creep resistance, up to 220°C, and excellent abrasion and friction behavior. Besides excellent fuel and oil resistance, PA 46 has high resistance against high energy radiation, very low flash, and good electrical insulating properties [274].

Limitations of PA are low dimensional stability, a quite high water absorption, and poor chemical resistance to strong acids and bases. They require UV stabilization to prevent degradation, can be attacked by oxidizing agents, and have high notch sensitivity [275]. PA is a flammable material and burns easily when and if it is exposed to an open flame [276]. PA 12 compared to other commercial PAs has lower stiffness, UV and heat resistance, and is more expensive. PA 46 needs higher temperature when processing, due to its high melting point, has low dimensional stability, and darkens with exposure to high heat [274]. Typical properties of generic PA polymers are presented in Tables 14.23 and 14.24.

There are many types of PA available as a homopolymer, copolymer, or reinforced. PA may also be blended with other engineering plastics to improve certain aspects of performance [256].

14.3.3.4 Processing

PA can be drawn, cast, or extruded. It is processed using injection molding, rotational molding, casting, or extrusion into film or filament [256]. When cold-drawn, it is tough, elastic, and strong. The most known form are filaments used in hosiery, parachutes, and bristles. PA is also used in molded form, particularly in injection molding, where its toughness and ability to flow around complicated inserts are prime advantages [256]. Thanks to their crystalline structure PAs are easy to inject, showing high fluidity, enabling precision at injection of thin-walled parts [274].

PAs may have a high or low melt viscosity depending on molecular weight, composition, and other factors. In extrusion process fiber and molding grade PAs can be used. Fiber grade, highly fluid resins are used in monofilament and wire coating applications.

Processing conditions for extrusion according to Ref. [274] are:

- maximum allowable moisture content: 0.1%,
- melt temperature: 230–290°C,
- compression ratio: <4.0,
- screw design (L/D ratio): 25–30.

TABLE 14.23 Typical properties of generic PA 6 and PA 66 polymers.

	PA 6	PA 66
Density (g/cm^3)	1.07–1.15	1.08–1.14
Melt flow rate (MFR) (g/10 min)	5.9–10	12–50
Water absorption: 23°C, 50% RH (%)	2.5–3.1	1.2–3
Water absorption: 24 h, immersed (%)	0.85–2.1	0.86–1.5
Tensile strength: Yield (MPa)	44.5–91	49–91
Tensile strength: Break (MPa)	39.1–81.4	39.9–93
Tensile elongation: Yield (%)	1.5–7.5	1.5–6.5
Tensile elongation: Break (%)	0.5–50	0.7–51
Tensile modulus (GPa)	1.54–3.69	1.35–4.05
Flexural strength (MPa)	54.9–122.7	11–170.3
Flexural modulus (GPa)	1.55–3.1	1.7–3.4
Charpy notched impact strength (kJ/m^2)	0.9–10.5	1–10.7
Notched izod impact (kJ/m^2)	1.5–16.4	3.8–6.1
Rockwell hardness	70–120	80–121
Coefficient of friction	0.04–1.4	0.08–0.36
Deflection temperature under load: 0.45 MPa (°C)	136–192	179.5–239.5
Vicat softening temperature (°C)	193–205.5	198.3–253
Melting temperature (°C)	219–223	259.5–263
Thermal conductivity (W/mK)	0.231–0.778	0.202–0.692
Surface resistivity (Ohm)	10^2–$2.5 \cdot 10^{14}$	$2.7 \cdot 10^3$–$2.5 \cdot 10^{16}$
Volume resistivity (Ohm•cm)	2–$2.5 \cdot 10^{16}$	1–10^{17}
Dielectric constant	3.39–3.91	2.86–3.85
Gloss (%)	105–170	140
Haze (%)	0.5–5.4	3

Adapted from Refs. [277,278].

14.3.3.5 Applications

PA is one of the most popular plastics today. It is used in various industries like: transportation, electronics and electrical, consumer goods, building and construction, and packaging. It is of the most common polymers used as fibers in technical textiles, carpets, and apparel [258,283]. Recently, it is also used in 3D printing applications.

Both, PA 6 and PA 66 are widely used in many different markets and applications due to their excellent performance/cost ratios [274]. Because of good processability, PA 6 and PA 66 are used as an alternative to metal in automotive, where design flexibility as well as temperature and chemical resistance are of critical importance. In food packaging applications PA 6 and PA 66 offer very high puncture resistance, barrier resistance to oxygen, carbon dioxide and aromas, transparency, etc. The outstanding fatigue properties and high impact and mechanical strength of PA 6 and PA 66 contribute in sport and leisure applications. PA 66 is used for durable consumer and industrial goods, thanks to its easy moldability, colorability, good surface aspect, and excellent mechanical resistance. PA 66 is also used when PA 6 reaches its limit temperature or when the hydrolytic stability of PA 6 is not sufficient anymore. It provides good surface appearance and weld strength leading to burst pressure resistance [256,274].

PA 12 is ideal for applications where safety, durability, or reliability over time is critical. Its remarkable long-lasting performance allows use in a wide range of conditions (temperature, pressure, chemical) [274].

TABLE 14.24 Typical properties of generic PA 12 and PA 46 polymers.

	PA 12	PA 46
Density (g/cm^3)	0.85—1.1	1.18—1.19
Melt flow rate (MFR) (g/10 min)	1—21	
Water absorption: 23°C, 50% RH (%)	0.48—0.72	2—3.7
Water absorption: 24 h, immersed (%)	0.57—0.71	0.6—13.5
Tensile strength: Yield (MPa)	23.7—50.7	99.3—100
Tensile strength: Break (MPa)	29.4—61	65—197
Tensile elongation: Yield (%)	4.7—6.9	5—55
Tensile elongation: Break (%)	0.75—200	39—280
Tensile modulus (GPa)	0.36—2.07	3.18—3.45
Flexural strength (MPa)	18.1—62.3	103.5—112.5
Flexural modulus (GPa)	0.11—1.65	3—3.03
Charpy notched impact strength (kJ/m^2)	2.5—9.9	5.7—11.1
Notched izod impact (kJ/m^2)	3.6—6.5	9.9—11.8
Rockwell hardness	59—105	90—100
Coefficient of friction	0.06—0.38	0.2—0.6
Deflection temperature under load: 0.45 MPa (ºC)	66.7—150	279—281
Vicat softening temperature (ºC)	129.5—178	250—290
Melting temperature (ºC)	169—178.5	290—295
Thermal conductivity (W/mK)	0.245—0.317	0.3—0.303
Surface resistivity (Ohm)	10^3—10^{13}	10^6—10^{16}
Volume resistivity (Ohm•cm)	10^2—10^{15}	10^{13}—1^{15}
Dielectric constant	2—17	3.2—22
Transmittance (%)	80—90	
Haze (%)	0.7	

Adapted from Refs. [279—282].

PA 46 is as a high temperature PA often used to replace metal in demanding, high temperature applications, i.e., in automotive and transportation and industrial goods. It provides excellent performances across a broad range of applications, such as consumer goods, safety controls in appliances [274].

14.3.3.6 Recycling

Though already in 1944, the recycling process of PA 6 carpets was devised by DuPont, there are relatively few recycling facilities that recycle PA, mainly due to the technical challenges that are common to its recycling. In the United States the Carpet Reclamation Program by DuPont processes more than 700 t of carpet each month. From 10 t of carpet waste 0.8 t of recycled PA 6 and 1 t of PA 66 can be obtained [284]. PA 6 can be recycled in three different ways, by mechanical, chemical, or thermal recycling. Thermal recycling involves only energy recovery during incineration of the polymer waste. Mechanical recycling or remelting leads to partial depolymerization of polymer, whereas chemical recycling disintegrates the long polymer chain into monomers that can be polymerized again, converting the waste into products with the quality of the virgin polymer. PA 6 can be depolymerized into its monomer caprolactam by acidolysis, aminolysis, hydrolysis, or catalyzed depolymerization in vacuum. Recycled PA 6 can be used in different applications: carpet cushioning and flooring material, highway noise abatement panels, automotive parts, roofing shingles, composite lumber, as well as in apparel [284].

In mechanical recycling PA 66 is melted and made into pellets to be used for injection molding of engineering components. However, this type of recycling always results in loss of quality [285]. Chemical recycling of PA 66 is not as easy as chemical recycling of PA 6. Company DuPont has developed a process that depolymerizes any mixture of PA 6 and PA 66 using ammonia. Ammonolysis involves heating PA with ammonia at elevated pressures in the presence of a Lewis acid to yield caprolactam and hexamethylenediamine for manufacture of PA 6 and PA 66, respectively [285].

Recently, studies of recycling PA 12 in additive manufacturing emerged. Hussainova and Veinthal reported reusing polymeric material left over from selective laser sintering (SLS) processes for making raw material for FDM processes [286]. Dung Ha studied reuse of PA 12 powder from 3D printing Multi Jet Fusion (MJF) by manufacturing 3D printing filament [287].

14.3.3.7 3D printing

PA can be easily melted into filaments and because of its good fluidity 3D printing filament prints very nicely. Among all the materials currently available for FDM, PA has the most versatile list of properties [288]. It contains no harmful pollutants or heavy metals, and no unpleasant odor while printing [288].

PA filaments typically require extruder temperatures near 250°C; however, some varieties allow printing at temperatures as low as 220°C.

Print settings for PA according to Refs. [274,289] are:

- print temperature: 225−265°C; 220−270°C,
- bed temperature: 110°C; 75−90°C,
- print speed: 30 mm/s is ideal (up to 80 mm/s); 40 mm/s,
- bed adhesion: PVA based glue on a glass or metal print bed,
- cooling fan: not required,
- enclosure: recommended.

Due to its moisture sensitivity, PA requires efficient drying process. Thus filament storage is very important and requires special attention. Before printing, predrying a filament is recommended. The drying process can be done in an oven at 70−80°C, for 4−6 h [289]. PA 12 absorbs water at half the rate of PA 6 or PA 66, making PA 12 with its lower absorption more favorable choice [288]. Delamination can also be caused by moisture, though it is usually consequence of not being printed hot enough.

PA is known as a tough, but also partly flexible, material that offers high impact and abrasion resistance, and as such being an ideal choice for printing durable parts [271]. Because of their high tensile strength PAs are used for 3D printed models for high heat applications instead of ABS [276]. When printed with higher density infill and wall thicknesses a very strong part that can handle significant shock and has excellent impact resistance is obtained. However, when printed thin wall structure it becomes very flexible [288]. The layer adhesion is excellent in producing fault-free prints. As details are reproduced well, small or intricate prints can be produced. PA 3D filament has a very low friction coefficient and does not need lubrication. It is ideal for production of moving parts. The finish quality is good, with very few rough edges after the print is complete resulting in a smooth silky finish with little need for postprocessing.

PA is hygroscopic material and readily absorbs moisture from its surroundings. Typically, it can absorb 10% of its density of water in just 24 h. Printing PA after it has absorbed water will lead to several print quality issues, to poor print finishes, or even popping in the extruder. The surface of the water exposed print is unaesthetic, with wispy stringing on the surface instead of smooth sheen. Due to material degradation, initiated by heat and water prints have also lower mechanical properties [288]. Natural PA has most commonly an off-white color and it is also commonly available in white and black, though it can be dyed into virtually any color. Because of high water absorption rate, PA can be easily colored/dyed [276]. PA can also be combined with a large variety of additives to produce different variants with significantly different material properties.

Advantages and disadvantages of PA, together with some tips for 3D printing, are presented in Table 14.25.

Compared to PA 66 the PA 6 exhibits similar stiffness at temperature below 180°C, better hydrolytic stability, and long-term heat aging. PA 6 has a slightly lower temperature resistance versus PA 66 and is also slightly less expensive. PA 66 is used when PA 6 reaches its limit temperature or when the hydrolytic stability of PA 6 is not sufficient anymore [274]. PA 6 has excellent strength and stiffness while maintaining good impact resistance (Fig. 14.13). It fills the niche between the more flexible PA 12 and the high rigidity of PA 12 reinforced with CFs. This combination makes it a good choice for tooling that can handle the rigors of a production environment [291]. In Table 14.26 some properties of 3D printing PA filaments and in Fig. 14.13 3D-printed objects from PAs are shown.

PA 12 is extremely tough with superior tensile strength, elongation at break, impact strength, and high fatigue endurance (Table 14.26). It is extremely stable both thermically and chemically and has superior UV resistance.

TABLE 14.25 Advantages and disadvantages of PA.

	PA
PROS	• Tough and partially flexible • High fatigue and impact resistance • High damping capacity • Excellent durability • Good abrasion resistance • No unpleasant odor while printing • Large color palette available • Inexpensive
CONS	• Extremely hydrophilic • Brittle at low temperatures • Prone to warping • Improperly dried filaments can cause printing defects • Not suitable for moist and humid environments • Can (potentially) shrink during cooling, so builds may be less precise
TIPS	• Warping can be avoid by using heated bed, applying PVA glue to the surface and without using cooling fan. • For good adhesion on the print bed PVA glue, PI tape, or synthetic resin bonded cotton fabric, known as Tufnol sheet, is used. • The most common way of drying a filament before printing is in a convection oven. • Requires more work to set up printer.

Adapted from Refs. [277,289,290].

FIGURE 14.13 3D-printed objects from (A) PA and (B) PA 6/PA 66. *(A) Image credits: Fillamentum Manufacturing Czech s.r.o. (B) Image credits: Ultimaker B.V.*

Compared to other PAs it has very low moisture absorption before and after printing and very low warping. It is perfect for production of ultrahigh-resistance functional parts. It is good choice for applications involving snap-fit closures, tools with press-fit inserts, components subject to high vibration, and parts requiring threaded inserts [292].

TABLE 14.26 Properties of 3D printing PA filaments.

	PA 6	PA 6/66	PA 12
Density (g/cm^3)		1.05	1
Melt flow index (g/10 min)		12	
Tensile strength: Yield (MPa)	49.3		32
Tensile strength: Break (MPa)	67.6	33.2	46
Tensile elongation: Yield (%)	2.3		2.4
Tensile elongation: Break (%)	38	143	30
Tensile modulus (GPa)	2.23	0.39	1.28
Flexural strength (MPa)	97.2	17.7	67
Flexural modulus (GPa)	2.19	0.45	1.27
Notched izod impact (J/m)	106	680	135
Deflection temperature under load: 0.45 MPa (°C)	93	65	97
Melting temperature (°C)		195–197	178

Adapted from Refs. [291–293].

Due to PA 46's excellent mar and wear resistance, it is used in gear applications where it offers a combination of mechanical and constant performances at high temperature, excellent tribological behavior, and high fatigue resistance. Due to its high fluidity, PA 46 is a good solution for complex shapes and parts with thin walls [274].

14.3.4 Polyesters

14.3.4.1 Development

PESs are family of engineering polymers that contain the ester functional group in their main chain [294]. The most common variety is polyethylene terephthalate (PET, PETE). Other types of aromatic PESs are polytrimethylene terephthalate (PTT, PETT) and polybutylene terephthalate (PBT). Polyethylene terephthalate glycol (PETG) is glycol-modified copolyester.

Saturated PESs were first studied by Carothers and his team (DuPont) in 1929. They produced thermoplastic PESs from propylene glycol and 1,16-hexadecanoic acid with an average molecular weight of $12\cdot10^3$, from which they could pull fibers. They dropped the work and carried on with the PA instead [16,295]. Later on studies on PESs were done by Whinfield and Dickson from Calico Printers Association. In 1941 they patented PET from the reaction of polyethylene glycol with terephthalic acid [295]. Terylene (PET) fibers were introduced by ICI in 1947, and later as film Melinex. In the late 1950s, researchers found a way to stretch a thin extruded sheet of PET to create PET film [296]. Molding powder was not generally available until the 1960s [295]. In the early 1970s, the technology was developed to allow for the blow-stretch molding of PET into bottles. In 1973, the PET bottle was patented and in 1977 oriented controlled structure blow molded bottles were introduced in the United States [295,296].

The first PBT fibers were produced in 1942 and the PBT compounds for molding were launched in the 1970s [297]. PTT was first synthesized and patented in 1941 by Whinfield and Dickson. The commercialization began later, when more economical and efficient methods to produce 1,3-propanediol was developed: in the 1980s by Degussa, via acrolein, and Shell via the hydroformylation of ethylene oxide [298].

14.3.4.2 Chemical structure and synthesis

PET is derived from benzene-1,4-dicarboxylic acid, crystalline solid obtained from xylene, and ethane-1,2-diol, a colorless liquid obtained from ethylene. The structure-based name for PET is poly(oxyethane-1,2-diyloxyterephthaloyl) [22]. The IUPAC name for PET is poly(ethylene terephthalate) or poly(ethylbenzene-1,4-dicarboxylate). Chemical formula is $(C_{10}H_8O_4)_n$ and molecular weight of repeat unit is 192.2 g/mol [299,300].

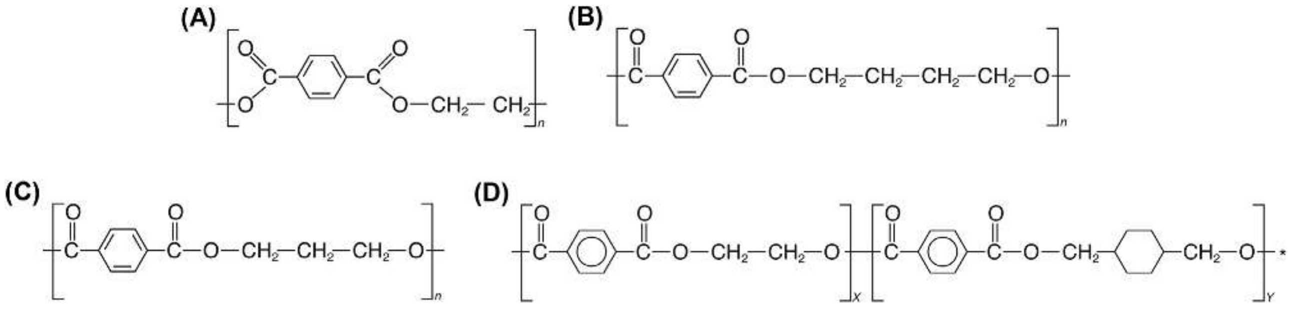


FIGURE 14.14 Repeat units of: (A) PET, (B) PBT, (C) PTT, and (D) PETG.

PBT is a saturated polyester obtained from 1,4-butanediol and terephthalic acid or dimethyl terephthalate. The structure-based name is poly(oxy-1,4-butanediyloxycarbonyl-1,4-phenylenecarbonyl). Chemical formula is $(C_{12}H_{12}O_4)_n$ and molecular weight of repeat unit is 220.23 g/mol [299,301].

PTT is made of terephthalic acid with 1,3-propanediol. Structure-based name is poly(oxy-1,3-propanediyloxycarbonyl-1,4-phenylenecarbonyl). Chemical formula is $(C_{11}H_{10}O_4)_n$ and molecular weight of repeat unit is 206.2 g/mol [299,302].

PETG is glycol-modified copolyester, containing less than 50% of 1,4-cyclohexanedimethanol (CHDM), a disubstituted derivative of cyclohexane, introduced to PET. Chemical formula of glycol-modified copolyester PETG is $(C_{10}H_8O_4 \cdot C_{16}H_{18}O_4)$ [299,303]. In Fig. 14.14 repeat units of different PESs are shown.

Synthesis of PESs is an example of a condensation polymerization. PET polymer are produced from ethylene glycol (EG) and either dimethyl terephthalate (DMT) or terephthalic acid (TPA). At both processes first the intermediate bis-(2-hydroxyethyl)-terephthalate (BHET) monomer is produced either by the esterification reaction between TPA and EG with water as a by-product, or by transesterification reaction between EG and DMT with methanol as a by-product [304]. The BHET monomer is then polymerized under reduced pressure with heat and catalyst to produce PET polymer. To avoid the need to recover and purify the methanol and to eliminate the potential VOC emissions, the TPA process is preferred [305]. Both, batch and continuous processes are used to produce PET using DMT.

Molten PET can be extruded directly through spinnerette, forming PES filaments or to form block, which are then cut into chips for later processing as a plastic [305]. In production of high molecular weights, as is the case for injection molded grade PET resins, the polymerization is carried out in stages: crystallization, annealing, solid-state polymerization, and cooling [306].

In a process of producing PBT, a mixture of BDO and TPA is esterified, and the esterification product is polycondensated. A process for the continuous preparation of PBT from TPA and 1,4-butanediol comprises:

(a) direct esterification of TPA with 1,4-butanediol in the presence of a catalyst solution,
(b) precondensation of the esterification product obtained in first stage, and
(c) polycondensation of the precondensate [307].

PTT is an aromatic PES synthesized by the transesterification of propanediol with DMT or by the esterification of propanediol with TPA in the presence of catalyst under a pressure of 70–150 kPa at a temperature of 260°C. The selection of the catalyst plays a major role on the reaction rate and PTT properties [308].

PETG is made using a two-step, melt-phase polycondensation process. The first step is esterification of TPA, EG, and 1,4-cyclohexanedimethanol at the temperature of 230°C in a nitrogen atmosphere in the presence of a metal catalyst, usually cobalt. The second polycondensation step is carried out at the temperature around 280°C under high vacuum [309].

14.3.4.3 Characteristics

PESs are thermoplastic semicrystalline polymers. The crystallinity of PET varies from amorphous to fairly high crystalline, depending on its processing and thermal history [310]. The presence of an aromatic ring in the PET repeating unit gives the polymer notable stiffness and strength, and makes it highly resistant to deformation [311]. PET is a hard, stiff, strong, dimensionally stable material, with very good strength to weight ratio. It doesn't break or fracture, and is practically shatter-resistant. It absorbs very little water and is known for its good gas (oxygen, carbon dioxide) and moisture barrier properties. Besides excellent electrical insulating properties, PET has good chemical resistance, except to alkalis. Resistance to alcohols, aliphatic hydrocarbons, oils, greases, and diluted acids is excellent, while to diluted alkalis, aromatic and halogenated hydrocarbons moderate. It is known for its broad range of use temperature, from −60 to 130°C [310]. PET can be highly transparent and colorless, also depending on thickness, thicker sections are usually opaque. Color can also be added [312]. Blending with various additives such as nucleating, antimicrobial, enzymes, colorants, cross-linking, matting agents or with other polymers results in different properties, and enables the applications in various fields [313]. PET is approved as safe food contact material by the FDA, Health Canada, EFSA, and other health agencies.

PBT has lower strength and stiffness than PET, and better impact resistance, so its mechanical and stain-resistant properties are excellent. Similar as PET, it is resistant to diluted acids, solvents, oils, and greases. It has high heat-deflection temperature, though lower than PET, resulting in high heat resistance (up to 150°C). PBT provides good creep resistance, dimensional stability, and low moisture absorption characteristics, blocks UV radiation, and has excellent heat aging behavior and resistance to environmental changes. It has extremely high electrical resistance and high dielectric strength. PBT meets regulatory approvals for food, medical, and potable water applications [314,315].

PTT has excellent properties including good tensile behavior, resilience, outstanding elastic recovery, and dyeability, which make it an ideal candidate for use in applications such as textile fibers, carpets, or as an engineering plastic [316–318]. PTT combines the chemical resistance characteristics from a PES with the elastic recovery and resilience of PA. PTT also offers inherent stain resistance, and is continuously printable and dyeable without speciality chemicals in a full color range [316–318]. It has excellent flow and surface finish and a good color fastness against UV light, ozone, and NOx [316–318]. PTT provides lower water absorption and has the potential to be recycled. Compared to PBT, PTT exhibits better tensile strength, flexural strength, stiffness, shows more uniform shrinkage and better dimensional stability. It can also be more cost effective [316].

PETG offers a desirable combination of properties such as clarity, toughness, and stiffness. PETG is strong, can be rigid to semirigid, depending on the thickness, and exhibits relatively higher impact-resistant as compared to PET. It is colorless and exhibits relatively higher transparency; it has exceptional water and moisture barrier properties. PETG has higher resistance to heat sealing, ETO, and gamma sterilization processes compared to PET [319,320]. The presence of glycol in the polymer structure helps to prevent the visible hazing, warping, and crystallization effects that typically arise with PET. This, together with the resistance to brittleness means that PETG has a slightly softer surface, making it more pliable and highly impact resistant, although the risk for damage from scratches and UV light is higher for PETG [321].

PESs have some limitations that limit their applications. Some of disadvantages are lower chemical resistance to alkalis, strong bases and hydrocarbons, also to ketones, and diluted acids and alkalis at high temperatures higher than 60°C [312,314,316]. They are also affected by boiling water. PET has lower impact strength than PBT, whereas PBT has lower strength and rigidity than PET, and PTT has lower impact strength than PET and PBT [312,314,316]. PBT has lower Tg than PET and is more prone to warp. PET has lower moldability than PBT, due to its slow crystallization rate [312,314]. Limitation for PESs is also its poor burning behavior.

Typical properties of generic PES polymers are summarized in Tables 14.27 and 14.28.

14.3.4.4 Processing

In semicrystalline form, PET is made into a high-strength textile fiber with excellent resistance to wrinkling in fabrics. It can be processed by injection molding, extrusion, blow molding, and thermoforming into a high-strength plastic that can be shaped by different methods [311]. PET is generally extruded to produce films and sheets. It is also blow-molded into transparent containers of high strength and rigidity that are also impermeable to gas and liquid [311]. To process PET by either extrusion or injection molding, the moisture content has to be below 0.02% to prevent hydrolysis during processing, which can be achieved with drying for 4 h at 150°C [47].

PBT is processed mainly by injection molding but it can also be processed by extrusion, blow molding, monofilament extrusion, melt blown, and spunbond production. It has a relatively small processing window, with the recommended melt temperature between 243 and 266°C, whereas at PET recommended melt temperature is 270–300°C [47].

PETG is a clear amorphous thermoplastic which can be injection molded, sheet extruded, and blow molded. PETG can be processed over a wider processing range than conventional PET [319]. Processing conditions for extrusion of PET, PBT, and PETG are given in Table 14.29.

14.3.4.5 Applications

PET is used in diverse applications, mainly for textiles and food packaging. The majority of the PET production is for synthetic fibers (60%), followed by the bottle production (30%) [40]. PET is the most important man-made

TABLE 14.27 Typical properties of generic PET and PBT polymers.

	PET	PBT
Density (g/cm^3)	1.39–1.4	1.29–1.32
Melt flow rate (MFR) (g/10 min)	14–60	3–45
Water absorption: 23°C, 50% RH (%)	0.2–0.5	0.2–0.25
Water absorption: 24 h, immersed (%)	0.4–0.7	0.04–0.5
Tensile strength: Yield (MPa)	54.3–84.8	39.1–60.9
Tensile strength: Break (MPa)	23.4–25.9	32.6–63
Tensile elongation: Yield (%)	4–4.1	3.1–11
Tensile elongation: Break (%)	14–250	1–56
Tensile modulus (GPa)	2.3–2.48	1.93–3.06
Flexural strength (MPa)	80.7–121.4	66.3–91.7
Flexural modulus (GPa)	1.1–2.21	1.99–2.97
Charpy notched impact strength (kJ/m^2)	2–6.9	1.5–10.3
Notched izod impact (kJ/m^2)	3.6–5	2–10.7
Rockwell hardness	104–126	71–120
Coefficient of friction	0.19–0.4	0.12–0.41
Deflection temperature under load: 0.45 MPa (°C)	66–68.5	114.5–174
Vicat softening temperature (°C)	74–85	158.5–220
Melting temperature (°C)	240–255	224.5–225
Thermal conductivity (W/mK)	0.015–0.29	0.245–0.274
Surface resistivity (Ohm)		10^2–$2.5 \cdot 10^{15}$
Volume resistivity (Ohm•cm)	10^3–$2.5 \cdot 10^{16}$	10^2–$2.5 \cdot 10^{17}$
Dielectric constant	3.38–3.81	3.2–3.41
Transmittance (%)	87.5–90.1	90
Haze (%)	0.25–4.93	1

Adapted from Refs. [322–324].

fiber, known as Polyester. It is used in apparel industry, home textiles and carpets, fiber filling for insulated clothing, furniture and pillows, industrial textiles, and nonwovens [311]. Besides manufacturing of water and carbonated-beverage bottles, PET is used for jars for food processed at low temperatures, trays and blisters, films and laminates in food packaging, as well as rigid cosmetic jars, cosmetic and pharmaceutical bottles and containers, microwavable containers [311,312,330]. It is widely known in the form of biaxially oriented and thermally stabilized films used for capacitors, graphics, backing for pressure sensitive adhesive tape, magnetic recording tapes, photographic film, balloons, etc. Other applications are in automotive, electrical, and electronic industry [310,311,315].

PBT can be processed into fibers for production of apparel and sportswear. It is mainly used in automotive, consumer goods, as well as electrical and electronics. It can be found in both automotive exterior and interior parts, consumer goods applications especially in small handheld appliances and tools, office, and sport equipment. PBT is used as an insulator in the electrical and electronics industries, due to its extremely high electrical resistance and high dielectric strength that help protect electrical and electronic components. Because of high mechanical strength PBT is also suitable for different industrial applications [314].

PTT is a viable and economical alternative to other PESs, and is used in textiles in clothing applications, home furnishing, carpets, nonwovens, automobile upholstery. It is also used as engineering plastic, for example, as injection molded parts in automotive [331].

TABLE 14.28 Typical properties of generic PTT and PETG polymers.

	PTT	PETG
Density (g/cm^3)	0.12–1.51	1.27–1.29
Melt flow rate (MFR) (g/10 min)	7–20	34–39
Water absorption: 23°C, 50% RH (%)	0.11–0.34	0.12
Water absorption: 24 h, immersed (%)	0.08	0.13–0.2
Tensile strength: Yield (MPa)	35–60	49.8–50.3
Tensile strength: Break (MPa)	41.1–180	25.9–29.1
Tensile elongation: Yield (%)	5–6	4–8.4
Tensile elongation: Break (%)	1–15	120–180
Tensile modulus (GPa)	1.6–29	1.1–2.2
Flexural strength (MPa)		68.9–73.8
Flexural modulus (GPa)	1.6–24.8	1.22–2.17
Charpy notched impact strength (kJ/m^2)	4–22	3.1
Notched izod impact (kJ/m^2)	4.5–5.5	2.7–4.6
Rockwell hardness		105–108
Coefficient of friction		0.22
Deflection temperature under load: 0.45 MPa (°C)	75–226	60–99
Vicat softening temperature (°C)		73–85
Melting temperature (°C)	227–229	
Thermal conductivity (W/mK)	0.2	0.21–0.29
Surface resistivity (Ohm)	10^5–$6 \cdot 10^{14}$	10^3–10^{16}
Volume resistivity (Ohm•cm)		$< 10^{15}$
Dielectric constant	3.4–4.3	2.4–2.6
Transmittance (%)		82–91
Haze (%)		0.2–1

Adapted from Refs. [325–327].

TABLE 14.29 Processing conditions for extrusion of PET, PBT, and PETG.

	PET	PBT	PETG
Predrying	Required	Required	Required
Melt temperature (°C)	270–290	235–250	246–274
Compression ratio	2.5:1	3:1	
Screw design (L/D ratio)	24–30	20–30	At least 24

Adapted from Refs. [312,328,329].

PETG has a wide range of applications, among others, in food and beverages industry, medical, cosmetic, and pharmaceutical packaging. It is used in manufacture of liquid containers, as well as in certain other packaging and thermoforming applications. The ability of PETG to resist rigorous ETO sterilization processes enables its use for sterile barrier applications in medical devices and pharmaceuticals packaging. PETG is suitable for higher temperature processes such as radiofrequency sealing, heat sealing, and other procedures required by blister packs and clamshells [117]. It is also used for 3D printing.

14.3.4.6 Recycling

PET products are 100% recyclable, and PET is the most recycled plastic worldwide. Recycling process starts with sorting. From sorted baled PET products, bottles are singulated. They are prewashed and labels removed, using steam and chemicals, because this process allows for easier identification of material using NIR sorting equipment to remove other materials. PET material is then ground into particles known as "flakes". Further separation techniques involve washing at standard or elevated heat levels and air classification as well as water baths, where material either sinks or floats, which helps separate residual foreign materials. After the completion of grinding, washing, and separation, the material is rinsed to eliminate any remaining contaminants or cleaning agents. The recycled PET (rPET) is then dried before further processing. Extruded material passes through a series of screens to form pellets while nonmelted particulate is blocked [332].

Low diffusion coefficient makes PET much more suitable than other plastic materials for use as a recovered, recycled material. Polymer rPET is employed for new products such as: carpet or apparel fiber, shoes, luggage, upholstery, fiberfill for sleeping bags and winter coats, industrial strapping, protective packaging, sheet and film, automotive parts, containers [312,332].

Chemical recycling is complementary to mechanical recycling, though it is more expensive. Usually by means of solvolytic chain cleavage, this process can either be a total depolymerization back to its monomers or a partial depolymerization to its oligomers and other industrial chemicals. PET can be cleaved by water, alcohols, acids, glycols, and amines. Three main methods in PET chemical recycling are glycolysis, methanolysis, and hydrolysis [333].

PETG is also recyclable, but recently concern has grown over the recycling of PETG with PET. PET and PETG require different processing temperatures during mechanical recycling and can act as contaminants for each other when recycled in the same stream [334]. When they are processed together, PETG melts and becomes sticky while PET remains solid. PETG sticks to PET chips and forms large clumps that pose processing problems. By adjusting the sensitivity of the NIR sorter at the beginning of the process PETG can be differentiated from PET and sorted out [335].

14.3.4.7 3D printing

In general, PET filament is an easy material to use for 3D printing. It combines the ease of use of PLA filament with the strength and durability of ABS filament. The temperature range for printing PET is quite wide, from 160 to 210°C, depending on type and additives. It is recommended to use a nozzle with a higher width diameter; however, printing with a 0.4 mm nozzle is often used. PET is not prone to warping; however, this filament flows well, consequently some oozing may be observed. Normally, a consistent diameter without bubbles is obtained. It is known for easy adhesion and will easily stick to heated beds, glass, or blue painter's tape [336]. There can be some trouble printing materials that have a lot of retractions.

The raw PET, PBT, and PTT are rarely used in 3D printing; the most popular 3D printing filament is PETG. Incorporating CHDM monomers greatly reduces the crystallinity of PETG which results in PETG having a significantly lower Tg and printing temperature than PET. PETG retains many of the desirable mechanical and chemical properties of PET while being much easier to print with [303]. PETG has a print speed slightly slower than that of ABS or PLA. Print speed is often in the range of 30 mm/s to 90 mm/s; however, this may vary depending on the filament and the printer, it is often not likely to go above 60 mm/s [303]. Recommended FDM print settings for PET and PETG are shown in Table 14.30.

3D-printed objects from PET have high flexibility and toughness [312,336]. PET is shockproof, hard material that is great to use for items that are lightweight. It is a crystal clear and colorless material; however, when heated or cooled its transparency changes. It has a glasslike appearance. High transparency and glossy surface finish are important qualities of PET. It is safe to use as food contact material and is waterproof, and has good chemical resistance [336]. Unlike ABS filament, it barely warps and produces no odors or fumes when printed. PET is also much more flame resistant than ABS and PLA [336].

Some of the major advantages of PBT are its excellent heat resistance for up to 150°C, resistance to solvents, and low shrinkage rate when forming. The material also has good electrical resistance. The addition of fibers (glass fibers (GFs)) enhances its mechanical and thermal properties. PBT is particularly suitable for technical applications that require high dimensional stability (electrical and electronic industry, automotive industry), as this material has a low coefficient of thermal expansion and a low water absorption [314,339].

PTT is more easily processable and less prone to moisture pick up than PET. Its mechanical properties are between those of PET and PBT and are slightly more rigid than PETG. PTT creates smooth, lustrous surface, and is popular for being transparent. It accepts pigments more easily than PBT and has outstanding color vibrancy [340].

TABLE 14.30 Print settings for PET and PETG.

	PET	PETG
Print temperature (°C)	210–230	220–250
Bed temperature (°C)	50–60	60–80
Print speed (mm/s)	40–80	30-90, up to 60
Bed adhesion	Glue stick, blue painter's tape	PEI, blue painter's tape, hairspray
Cooling fan	Required	Required
Enclosure	Not required	Not required

Adapted from Refs. [303,337,338].

PETG filament is more heat-resistant, flexible, and tough than PLA, but easier to print than ABS. It offers higher strength, lower shrinkage, and a smoother finish than PET. It is also clearer, less brittle, and easier to use than PET. PETG's flexibility, strength, and durability makes it an ideal 3D printing filament to be used for objects which might experience sustained or sudden stress, like mechanical parts, printer parts, and protective components [60,312]. PETG demonstrates very little shrinking so is suitable for printing large parts. It is slightly softer that PET, ABS or PLA making it more difficult to break but also more susceptible to wear, it scratches more easily than ABS. PETG is generally considered as food safe material [303].

PETG is resistant to water and has great chemical resistance. Nevertheless, it will absorb water from the air, which can lead to increased brittleness, filament breaking, bubbling when printing, or filament degradation. But, because it is hygroscopic and sticky during printing, this is good for layer adhesion [60]. Unlike ABS, PETG does not release foul odors during printing [341].

PETG is particularly prone to stringing and oozing when printing. It can also form droplets. The print temperature for PETG is generally between 220 and 250°C. If the printing temperature is too high, PETG may leak from extruder, and thin strings between different areas of print can build. If the printing temperature is too low then the layers of PETG will not adhere to each other properly. This may result in a rough surface or weak areas that can be easily pulled apart [303].

Some advantages and disadvantages of PET and PETG, printing tips, as well as some properties of 3D printing filament are given in Tables 14.31 and 14.32. In Fig. 14.15 PET printed objects and B-PET printing filaments are shown. B-PET is 3D printing filament made from recycled postconsumer PET bottles.

TABLE 14.31 Advantages and disadvantages of PET and PETG.

	PET
PROS	• Very strong, shockproof, and lightweight • Broad range of use temperature, from −60 to 130°C • Waterproof • Does not produce odor or fumes while printing • Transparent, glasslike appearance • Recyclable
CONS	• Affected by boiling water and alkalis • Hydrophobic • Has a wide range of printing temperature • May be slow to print • Poor bridging characteristics
TIPS	• Low extrusion temperature leads to poor layer adhesion. • Suggested initial printing speed: 30 mm/s for outlines, 60 mm/s for infill; a slower printing rate will reduce poor layer adhesion. • Suggested top/bottom thickness: 1.5 mm, or at least 6 solid layers. • For clear PET, printing at higher temperature is needed. • A more glossy/transparent look is obtained with increasing layer height to 0.2 mm or higher, printing at higher speed.

Continued

TABLE 14.31 Advantages and disadvantages of PET and PETG.—cont'd

	PETG
PROS	• Very strong • Flexible • Lower risk of warping • Low shrinkage • Glossy and smooth surface finish
CONS	• Quite high printing temperature and bed temperature • Sticky and stringing problems • Poor bridging characteristics • Clarity will make any imperfections within the internal layers visible • Less resistant to scratches than ABS
TIPS	• Thicker layers will make objects look more shiny and transparent. • Active cooling and slightly lower print speed and temperature can help to mitigate sagging. • Printing PETG directly onto glass should be avoided. • Moderate cooling with a fan is usually required; however, not cooling the first few layers ensures good adhesion.

Adapted from Refs. [303,312,336,338,342,343].

TABLE 14.32 Properties of 3D printing PET and PETG filaments.

	PET	PETG
Density (g/cm^3)	1.34	1.27
Water absorption: 23°C, 50% RH (%)	>0.015	0.13
Tensile strength: Yield (MPa)		50
Tensile strength: Break (MPa)	70	28
Tensile elongation: Break (%)	9	100
Tensile modulus (GPa)	2.3	2.1
Flexural strength: Yield (MPa)		68
Flexural modulus (GPa)		2
Notched izod impact (kJ/m^2)		6.2
Rockwell hardness		109
Deflection temperature under load: 0.45 MPa (°C)		70
Vicat softening temperature (°C)		85
Glass transition temperature (°C)	70	80
Melting temperature (°C)	214	
Thermal conductivity (W/mK)		0.21
Volume resistivity (Ohm•cm)	$>10^{16}$	10^{15}
Transparency (%)	90	91

Adapted from Refs. [337,344].

14.3.5 Polycarbonate

14.3.5.1 Development

PC is one of the high-performance heterochain polymeric materials that comprise the family of engineering thermoplastics. The reaction of polyhydroxy compounds with some carbonic acid derivatives results in a series of related polymers with carbonate (–O–(C=O)–O–) linkages, and these polymers are referred to as PCs [345].

First PCs were made in the reaction of phosgene with dihydric phenols by Einhorn in 1898, and in 1902 by Bishoff and Hedenstrom, using an ester-exchange reaction. These PCs were intractable, insoluble materials. In 1930

FIGURE 14.15 3D-printed objects from (A) B-PET printing filaments and (B) PETG. *(A) Image credits: B-Pet. (B) Image credits: Fillamentum Manufacturing Czech s.r.o.*

Carothers and Natta prepared a number of aliphatic PCs [16]. Hermann Schnell of Bayer produced linear thermoplastic PC of high molecular weight in 1953, just 1 week before chemist Daniel Fox of the General Electric Company made the same discovery while working on developing a new wire insulation material. Both companies applied for US patents in 1955 [346]. Soon after bisphenol A (BPA) became commercially available in 1956, BPA PC was developed [16]. PC was introduced in 1958 by Bayer AG of Germany and the full-scale production commenced in 1959 in Germany and 1960 in the United States [100].

14.3.5.2 *Chemical structure and synthesis*

BPA based PC is polymer made by the condensation of BPA ($HO{-}(C_6H_6){-}C(CH_3)_2{-}(C_6H_6){-}OH$), a volatile liquid derived from benzene and carbonic acid $HO{-}CO{-}OH$ or phosgene, a highly reactive and toxic gas made by reacting carbon monoxide with chlorine [347]. The atomic components building PC are carbon, hydrogen, and oxygen. The IUPAC name of PC based BPA is poly(oxycarbonyloxy-1,4-phenylenedimethylmethylene-1,4-phenylene). The molecular formula, shown in Fig. 14.16, and molecular weight of repeat unit are $(C_{16}H_{14}O_3)_n$ and 254.3 g/mol [71].

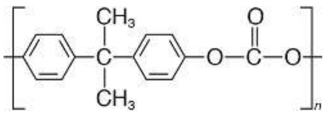


FIGURE 14.16 Repeat unit of PC.

PC is most often produced by the reaction of BPA and phosgene ($COCl_2$) in step-growth polymerization in which Cl^- ions are eliminated every time the monomers react. The resultant polymers are made up of repeating units containing two aromatic (benzene) rings connected by ester (CO−O) groups [348]. Another route to PC synthesis entails transesterification from BPA and diphenyl carbonate. This process results in more impurities, and is more expensive because higher temperatures are needed. But, the process is greener than phosgene method because the diphenyl carbonate is derived in part from carbon monoxide [349].

The chemistries employed to make PC polymer include interfacial, transesterification, and solution-based methods. The methods differ significantly in medium of reaction, monomeric raw materials, catalysts, temperature history, and special promotors. Solution PC synthesis was the first process pursued commercially. A solution of BPA in sodium hydroxide is prepared. It is mixed with a solution of carbonyl chloride in an organic solvent. The polymerization takes place at the interface between the aqueous and organic layers with the help of a catalyst. This solution is then run off from the aqueous layer and is either evaporated to form granules of the polymer or ethanol is added to precipitate the solid polymer [350].

The transesterification reactions are carried out in the melt phase. The condensation reaction results in the exchange of hydroxylic reagents with the diol releasing the monohydroxylic agent, which is removed by distillation leaving behind the polymeric molecules. The PC melt is then pressed through fine nozzles to form filaments, which are cooled down and granulated [350,351].

14.3.5.3 Characteristics

Transparency, excellent toughness, thermal stability and a very good dimensional stability make PC one of the most widely used engineering thermoplastics. PC is strong, stiff, hard, tough thermoplastic that can maintain rigidity up to 140°C and toughness down to −20°C [352]. It is unique in its working temperature and ability to experience minimal degradation between heating and cooling points [353]. It also has a high heat deflection temperature and absorbs very little moisture [354].

A very good heat resistance of PC combined with the flame-retardant materials results in stable material without significant degradation. Although they are made in a variety of colors, the raw material is highly transparent, transmitting approximately 90% of visible light [355,356]. PC has good chemical resistance against diluted acids, aliphatic hydrocarbons, and alcohols; moderate chemical resistance against oils and greases, but is readily attacked by diluted alkalis, aromatic, and halogenated hydrocarbons [357,358]. Typical properties of generic PC polymer are presented in Table 14.33.

There are also certain limitations associated with PCs, as low fatigue endurance and degradation of mechanical properties after prolonged exposure to water at over 60°C.

Constraints to the use of PC include limited chemical and scratch resistance and it is tendency to yellow upon long-term exposure to UV light. They are attacked by hydrocarbons and bases. When exposed to oils and fatty acids, this can cause stress cracking of parts [349]. PC can also craze when exposed to alcohols at high strains [357]. However, these constraints can be overcome with addition of right additives or blending [352,358].

14.3.5.4 Processing

PC can be processed by extrusion, injection molding, blow molding, thermoforming, vacuum forming, etc. There are two major techniques involved in PC processing: injection molding and extrusion [352,358]. Injection molding is most often used method to produce parts made from PC and its blends. In this process, the polymer melt is pressed into a mold with high pressure and at high melt temperature to reduce its viscosity. Since PC is a poor-flowing plastic, wall thickness should not be too thin. In the extrusion process melted polymer is forced through a die to produce flat sheets or profiles of various lengths, widths, and thicknesses with uniform cross sections [358].

Recommended processing conditions for extrusion according to Ref. [47] are:

- predrying: 2−4 h at 100−120°C,
- melt temperature: 227−260°C,
- cylinder temperature: 270−300°C,
- screw design (L/D ratio): 24−30.

PC is very pliable material. It can typically be formed at room temperature without cracking or breaking and can be reformed even without the application of heat [360]. This characteristic makes PC particularly useful in prototyping applications where sheet metal lacks viability (e.g., when transparency is required or when a nonconductive material with good electrical insulation properties is required) [356].

TABLE 14.33 Typical properties of generic PC polymer.

	PC
Density (g/cm^3)	1.19–1.20
Melt flow rate (MFR) (g/10 min)	1.8–24
Water absorption: 23°C, 50% RH (%)	0.066–0.18
Water absorption: 24 h, immersed (%)	0.14–0.2
Tensile strength: Yield (MPa)	54–67.5
Tensile strength: Break (MPa)	48.3–73.8
Tensile elongation: Yield (%)	3.8–7.5
Tensile elongation: Break (%)	1–150
Tensile modulus (GPa)	1.88–2.71
Flexural strength (MPa)	71.7–102
Flexural modulus (GPa)	1.88–2.60
Charpy notched impact strength (kJ/m^2)	7.6–82
Notched izod impact (kJ/m^2)	7.4–84
Rockwell hardness	68–120
Coefficient of friction	0.39
Deflection temperature under load: 0.45 MPa (°C)	129–141.7
Vicat softening temperature (°C)	136–150.5
Melting temperature (°C)	140–232
Thermal conductivity (W/mK)	0.173–0.721
Surface resistivity (Ohm)	$1–10^{16}$
Volume resistivity (Ohm•cm)	$1.6–2.5 \cdot 10^{16}$
Dielectric constant	2.7–3.01
Gloss (%)	15–98
Transmittance (%)	86.7–91
Haze (%)	−0.5–1.99

Adapted from Ref. [359].

14.3.5.5 Applications

High-performance properties of PC, such as outstanding impact resistance and dimensional stability, make PC the leading plastic material for various applications that demand high functioning temperatures and safety features [353]. PC and its blends are used in appliances, medical applications, automotive and transportation, building and construction, consumer products, electrical components, and also in 3D printing. It is commonly used for plastic lenses in eyewear, in medical devices, automotive components, protective gear, greenhouses, digital disks, and exterior lighting fixtures [356].

Because PC has an impact strength considerably higher than most plastics, it is fabricated into large carboys for water, shatterproof windows, safety shields, and safety helmets [352]. Because of its heat resistance and shatter resistance, PC is used in applications for direct contact with foods and beverages. Food storage containers made from PC are reusable, help preserve freshness, protect foods from contamination, and can be conveniently used in the refrigerator and microwave [358].

The characteristics of PC are similar to PMMA, but PC is stronger, useable in a wider temperature range [358]. In recent years, PC blends are becoming more important. Excellent compatibility with a range of polymers enables production of different blends, resulting in improved properties.

14.3.5.6 Recycling

PC is 100% recyclable; bottles and CDs are being extensively recycled already. After collecting the PC scrap, a quality assessment is made. Different types of PCs are sorted. The next step comprises feeding of the different shapes and forms of PC scrap into the various recycling machines; i.e., shredding, washing, and turning into a granulate [361].

Presently, postconsumer recycling of PC is common for applications where high volumes are available and no sorting is necessary. For all postconsumer PC waste, for which mechanical recycling has not proven to be economically feasible due to complex collection and/or dismantling steps, energy recovery is the best option [362].

One other method of recycling PC is by chemical recycling. PC reacts with phenol in the presence of a catalyst, BPA and DPC monomers are formed. After purification, both these monomers are used to produce the polymer [363].

As PC is made with BPA there exists some concern about the potential for low levels of BPA migration from PC packaging (material degradation in contact with water) into food and beverages. Several regulatory authorities worldwide have recognized safe use of PC for food contact applications, but there are some studies as well, which showed BPA to be a hazardous risk to health and hence, leading to development of “BPA-free” PC products [363].

14.3.5.7 3D printing

PC is a strongest thermoplastic material available in consumer 3D printing. It is a strong, durable, and tough material. Three main features of PC are optical clarity, resistance to heat, and incredible high toughness. It has extremely high heat deflection temperature, and maintains temperature and impact resistance [356,364]. Because of its high Tg (150°C) PC maintains its structural integrity up to that temperature [356,364]. 3D printable variants typically have a temperature resistance of just over 110°C, yielding translucent, icy prints [365].

It is a naturally transparent thermoplastic. Colors are usually limited to clear, white, and black. Clear printed parts usually require some postprocessing to remove tool marks and to restore the transparent nature of the material [364].

High heat resistance of PC is also problematic characteristic of 3D printable filament, as it is even more prone to warping and splitting, than ABS filament. As such, it needs high temperatures in order to extrude and have proper layer adhesion. Most available PC filaments contain additives that allow the filament to be printed at lower temperatures [366]. To print with PC, a 3D printer capable of managing high print temperature is needed; i.e., print temperatures of 290—315°C and print bed temperature up to 150°C. Enclosed print chamber to manage the heat and prevent imperfections in the printed part, such as cracking and deformation, is needed [367].

Tips for printing, as well as advantages and disadvantages of PC, are given in Table 14.34, whereas typical properties of 3D printing filament are given in Table 14.35.

Recommended 3D printing conditions according to Refs. [364—366] are:

- print temperature: 260—310°C,
- bed temperature: 80—120°C; 90°C or higher, up to 150°C,
- print speed: 30—40 mm/s; can go up to 60 or 80 mm/s,
- bed adhesion: PEI, PI tape with glue, blue painter’s tape with glue, buildtak,
- cooling fan: 10%—20%; 0%.
- enclosure: closed build chamber.

PC is extremely hygroscopic, meaning it will absorb moisture from the air, which will affect its printing performance and strength. Printing wet PC can lead to hydrolysis which will permanently alter the filament on a molecular level, making it significantly weaker. It also requires very high temperatures for printing and will exhibit layer separation if printed at too low temperature or with excessive cooling [364].

14.3.6 Thermoplastic polyurethane

14.3.6.1 Development

Thermoplastic elastomer (TPE) is defined as “a polymer blend or compound which, above its melt temperature, exhibits a thermoplastic character that enables it to be shaped into a fabricated article and which, within its design temperature range, possesses elastomeric behavior without cross-linking during fabrication” [370]. There are seven main groups of TPE, one of them is thermoplastic polyurethane (TPE-U or TPU). TPU is an engineering polymer that consists of linear segmented block copolymers composed of hard and soft segments. TPUs are subdivided into aromatic and aliphatic varieties.

TABLE 14.34 Advantages and disadvantages of PC.

	PC
PROS	• Excellent impact resistance • High toughness, even down to −20°C • High heat resistance (high mechanical retention up to 140°C) • Naturally transparent, very high transmittance • Good abrasion resistance • Bendable without breaking
CONS	• Low fatigue endurance • Low scratch resistant • Requires very high print temperatures • Prone to severe warping and layer splitting • High tendency to ooze while printing • Readily absorbs moisture • Mechanical properties degrade after prolonged exposure to water at over 60°C • Very energy-intensive printing process
TIPS	• Strong bed adhesion is essential for successfully printing. • The key to get a good first layer is in printer calibration and printing speed. It is recommended that an overall printing speed, including infill, should not exceed 20 mm/s. • To prevent stringing and oozing increasing the retraction distance and retraction speed are needed. • If parts are overheating, curling, or showing signs of drooping, the fan should be set to 0% for the first layer, and after forth or fifth layer the fan speed should be increased to 40% or below. • Retraction distance should be kept under 10 mm while printing. • If material is not dry, the printing temperature must be lowered to 280°C or below, to prevent artifacts or bubbles in the print, resulting from the moisture content. • Extruded filament tends to drop, if it is unsupported. Infill layers should be printed slowly, at around 50% speed, so that they have the best chance of successfully bridging the spaces between infill lines.

Adapted from Refs. [358,364,366].

TABLE 14.35 Properties of 3D printing PC filament.

	PC
Density (g/cm^3)	1.2
Melt flow index (g/10 min)	8.4
Water absorption: 23°C, 50% RH (%)	0.35
Tensile strength: Yield (MPa)	40–60
Tensile strength: Break (MPa)	57
Tensile elongation: Yield (%)	2.2–6
Tensile elongation: Break (%)	4.8–50
Tensile modulus (GPa)	2–2.3
Flexural strength (MPa)	90
Flexural modulus (GPa)	2.4
Notched izod impact (kJ/m^2)	80–89
Deflection temperature under load: 0.45 MPa (°C)	138
Vicat softening temperature (°C)	139
Thermal conductivity (W/mK)	0.2
Volume resistivity (Ohm•cm)	$6\cdot10^{13}$–$2\cdot10^{14}$
Dielectric constant	2.8–3
Transmittance (%)	89

Adapted from Refs. [368,369].

Otto Bayr is named the “father” of the polyurethanes (PUs) for his invention of the basic diisocyanate polyaddition process in 1937 [371]. At the beginning of World War II, PU was first developed as a replacement for rubber and was first used as coatings for impregnation of paper and textiles, and to protect metal, wood, and masonry [371]. By the mid-1950s, PU was also found in adhesives, elastomers, and rigid foams. During the late 1950s, moldable PU was produced [372]. TPU was developed by Lubrizol and the Estane brand TPU was patented and introduced in 1959 [373]. First application of TPU was as a replacement for PVC [374]. Later on, PUs were found to be useful for the production of plastics, elastomers, foams, adhesives, fibers, and corrosion-resistant coatings [16,375].

14.3.6.2 Chemical structure and synthesis

PU also known as polycarbamate is characterized by carbamate groups ($-NHCO_2$) in its molecular backbone, and is composed from hard and soft segments. The hard segment in TPU is isocyanate, aromatic or aliphatic; the soft segment is either a polyester or polyether type polyol [376]. Repeat unit of TPU (4,4′-methylenediphenyl diisocyanate (MDI)/1,4-butanediol (BD)) is shown in Fig. 14.17.

PUs that have important commercial uses typically contain also other functional groups in the molecule including esters, ethers, amides, or urea groups [372]. They are formed by reacting a polyol (HO−R−OH) with a diisocyanate (OCN−R−NCO) or a polymeric isocyanate in the presence of suitable catalysts and additives [371]. The hard segments of PU contain isocyanates like aliphatic (e.g., hexamethylene diisocyanate (HDI), 4,4′-methylene dicyclohexyl diisocyanate (HMDI)) or aromatic diisocyanates (e.g., 4,4′-methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), isophorone diisocyanate (IPDI)), as well as chain extender moieties (e.g., 1,4-butanediol (BD) or 1,3-propanediol)), whereas the soft segments are polyols moieties, like poly(tetrahydrofuran) (PTHF), poly(ethylene glycol) (PEG) [377]. TPU is a multiphase block copolymer manufactured primarily using: diisocyanates such as diphenylmethane diisocyanate (MDI), difunctional polyols with lower molecular weights, and chain extender, such as low-molecular-weight diols or diamines [373]. The diisocyanate and polyol react randomly to form soft segments while the diisocyanate and diol form hard segments. The average lengths of the hard and soft segments are governed by the starting amounts of the three ingredients [373].

In TPU polymer that is in a solubilized or melted state, mostly independent polymer chains are present. In the solid state they start to interact, which leads to the formation of hard segment domains that are organized in a somewhat spherical shape. Physical cross links through hydrogen bonding occur between hard segments of adjacent chains. The hard segment domains act as “virtual cross links” that reinforce the structure [373,378].

TPUs are mainly manufactured by bulk polymerization. They can be manufactured in one-shot polymerization, whereby the long-chain polyol, chain extender of short-chain glycol, and diisocyanate are all polymerized together; or by the prepolymer process whereby long-chain polyol and diisocyanate are first reacted to synthesize a prepolymer, short-chain glycol is then added and the mixture is polymerized [379].

Industrial production of TPU is carried out by batch processing, band casting, or reactive extrusion (REX). In REX process each of the reactants is fed into the extruder separately. The reaction then proceeds due to the elevated temperature and mixing which occurs within the extruder. The low viscosity liquid is transported to the extruder and polymerized while being mixed, affording a high viscosity polymer. After extrusion the material is pelletized [378,379].

14.3.6.3 Characteristics

TPU retains many of the advantages of PU while remaining melt processability, and exhibits properties somewhere between traditional rubber and plastic materials [378]. TPU reveals a numerous of physical property combinations and processing applications. It is highly elastic, flexible, and resistant to abrasion, impact, and weather [371]. According to type of polyol there are two major TPU classes: polyester TPUs and polyether TPUs. Within each class, selection of the specific diol and adjusting the ratios of the three ingredients leads to the TPUs ranging in hardness from about 70 Shore A to 70 Shore D and flexural moduli from 7 to 490 MPa [373].

TPU has good balance of mechanical properties and durability, including excellent wear and tear resistance, good chemical resistance, high resilience, low compression set and unique sound, and vibration dampening characteristics. Certain grades of TPU offer exceptional hydrolytic stability and low-temperature flexibility, while others

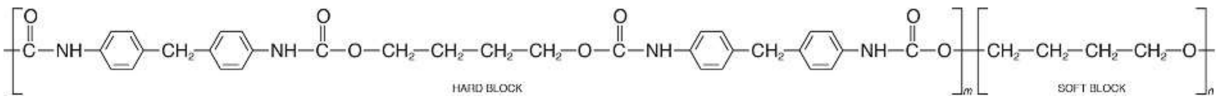


FIGURE 14.17 Repeat unit of TPU.

TABLE 14.36 Typical properties of generic TPU and TPE polymers.

	TPU	TPE
Density (g/cm^3)	0.938–1.24	0.828–1.21
Melt flow rate (MFR) (g/10 min)	0.8–5	0.2–21
Water absorption: 23°C, 50% RH (%)	0.4–0.5	
Water absorption: 24 h, immersed (%)	1.4	0.05–0.5
Tensile strength: Yield (MPa)	8.5–32	5–36
Tensile strength: Break (MPa)	22.7–61	
Tensile elongation: Yield (%)		55–930
Tensile elongation: Break (%)	250–840	38–90
Tensile modulus (GPa)	0.05–1.88	>0.01
Flexural strength (MPa)	1.51–110	3–37
Flexural modulus (GPa)	0.01–0.16	0.002–0.68
Notched izod impact (kJ/m^2)	3.4–14.1	
Durometer hardness	33–97	28–91
Deflection temperature under load: 0.45 MPa (°C)	60–120	40.5–112
Vicat softening temperature (°C)	63–144	55–205
Melting temperature (°C)	177–206	125–163
Thermal conductivity (W/mK)	0.18–0.37	
Surface resistivity (Ohm)	10^{12}–10^{15}	10^{3}–$8.8 \cdot 10^{14}$
Volume resistivity (Ohm•cm)	10^{7}–10^{15}	10^{2}–$2.3 \cdot 10^{16}$
Dielectric constant	5–6.5	2.06–2.48
Haze (%)		1–15.8

Adapted from Refs. [382–384].

provide significant strength and ductility [376]. TPU can be produced in a wide range of hardness grades. Beside high elasticity and flexibility over a wide temperature range, they have high elongation and tensile strength, excellent low-temperature, and impact strength, and maintain soft rubbery feel. They are ranked among the best for load-bearing capability and are good replacement for hard rubber [374,380]. Typical properties of generic TPU and TPE polymers are presented in Table 14.36.

TPU shows good resistance to ozone, oil, grease, many solvents, and abrasion, as well as excellent resistance to high-energy radiation [374]. It has limited resistance to acids and alkaline solutions, swells when exposed to saturated or aromatic hydrocarbons, aliphatic esters, and ketones. Aromatic TPU can yellow by exposure to UV radiation [380]. Other benefits of TPU are excellent colorability and pleasant tactile properties. Most commonly TPUs are colored using color granules (masterbatches), but also using coloring pastes, liquid colors, or pure pigments it is possible [381].

Polyester TPUs have the highest mechanical properties, and higher resistance to heat and mineral oils, whereas polyether TPUs have highest hydrolysis resistance, the best low-temperature flexibility and better resistance to microbiological degradation [382]. Polyether TPUs are commonly used in wet environments, and polyester TPUs are commonly used to resist oil and hydrocarbon [385]. TPU has compared to AB rubbers higher strength and a considerable better abrasion resistance, and compared to PET lower stiffness [386].

14.3.6.4 Processing

TPU is soft and processable when heated, hard when cooled. Properties of TPU can be altered by varying the type of polyol used, by adjusting the ratio of raw materials, by changing the reaction conditions under which processing takes place, or by using additives like UV stabilizers, mold release agents, and flame-retardants [380].

The most important processing techniques for TPU are: injection molding, extrusion, and blow molding. It can be processed on ordinary extrusion and injection, blow, and compression molding equipment. It can be vacuum-formed or solution-coated and is well suited for a wide variety of fabrication methodologies [371]. Before processing, drying to a moisture content of ≤0.05% is recommended in order to prevent blisters or streaks on the surface of the finished product [381].

The high plasticizing energy needed to melt TPU and high shear stress requires a high torque for the screw drive and long-compression-zone screws, to avoid fluctuations in the screw speed and thus nonuniform homogenizing [381]. Because of high melt viscosity, the speed of extruder and the temperature should be adjusted according to hardness of TPU. Too low temperature and/or high speed may cause shear degradation [387]. The melt temperature at extrusion depends on hardness and its melt range. Low nozzle temperatures result in matte surfaces and high temperatures in glossy surfaces.

Processing conditions for extrusion according to Refs. [382,388] are:

- predrying: 4 h at 80°C,
- melt temperature: 160–230°C,
- cylinder temperature: 140–210°C,
- screw design (L/D ratio): 25–30:1.

Depending on hardness also the annealing temperatures differ; at the TPUs with hardness of ≤92 Shore A the temperature should be 80–90°C, and for a hardness of ≥93 Shore A, 100–110°C [388].

TPU can also be welded, painted, printed, and die-cut. Printing techniques that can be used are hot embossing, ink-jet printing, pad printing, and laser printing. At machining excessive sharp cutting tools are needed, and the heat generation should be avoided [381].

14.3.6.5 *Applications*

TPU is a versatile material, due to its outstanding toughness, durability, or processing ease, that bridges the gap between rubber and plastics [371]. Aromatic TPUs based on isocyanates, like MDI, can be used in applications that require flexibility, strength, and toughness. Aliphatic TPUs based on isocyanates are light stable and are used in applications where optical clarity, adhesion, and surface protection are required. They are commonly employed in automotive interior and exterior applications and as laminating films [380].

Applications for injection molded TPUs are in automotive, medical, optical, electrical, wires and cables, coverings, protective cases like cellphones [389]. The combination of very good scratch and aging resistance and extremely fast cycling performance makes TPU very applicable for automotive market [390]. It is a popular material for use in tubing, medical devices, sporting goods, and other industrial products. It can also be compounded to create protective coatings or functional adhesives [374]. Highly breathable TPUs are used in sportswear, footwear, or building and construction products. Combination of high transparency with abrasion resistance and very good hardness are characteristics needed in production of transparent films, tubes, and hoses. TPU films are used as inflatables, textile coatings, garment, adhesive, and barrier films [390].

When mixed with the GF or mineral fillers, its abrasion resistance, paintability, high impact strength, and good low-temperature flexibility can be enhanced further [371]. Pure and blended TPU filaments have gained some popularity over the years also in 3D printing.

14.3.6.6 *Recycling*

Depending on the type of PU, different ways of recycling can be applied, such as grinding and reuse or particle bonding [391]. PU can be recycled in mechanical recycling process, in which the material is reused in its polymer form, or chemical recycling process into various chemical constituents. With regrinding or powdering industrial trim or postconsumer parts are grinded to produce a fine powder. The resultant powder is mixed with virgin materials to create new foam or reaction injection molded (RIM) parts. With the adhesive pressing/particle bonding PUs from various applications and industrial trim are used to create boards and moldings, often with very high recycled content. Used PU parts are granulated and blended, then formed into boards or moldings under heat and pressure. The resulting products are used in sound proofing applications, furniture that is virtually impervious to water and flooring where elasticity is needed [392]. In compression molding RIM and reinforced RIM parts are grinded into fine particles. With high pressure and heat they are molded creating products with up to 100% recycled content [392].

TPUs do not lose structural integrity when reprocessed multiple times. After second recycling TPU loses 25% on tensile strength, after forth recycling it has only the half of the strength. The clean, sorted scrap resulting from the processing of TPU can be recycled after appropriate treatment and drying. The proportion of recycled material should not, however, be more than 30% [381].

In the process of glycolysis mixed industrial and postconsumer PU is mixed with diols at high heat, causing a chemical reaction that creates new polyols. These polyols can retain the properties and functionality of the original polyols and can be used in myriad applications [392]. Hydrolysis creates a reaction between used PU and water, resulting in polyols and various intermediate chemicals. The polyols can be used as fuel and the intermediates as raw materials for PU. In the process of pyrolysis gas and oil are created. Similar to pyrolysis, hydrogenation creates gas and oil from used PU through a combination of heat and pressure and hydrogen [392].

If the materials can no longer be recycled, they should be incinerated in a waste incineration plant on account of their high calorific value, as it contains the same amount of energy as coal [381]. If disposed of in municipal landfill sites, they normally do not constitute a hazard to water, though this can depend on raw materials used in processing the TPU. Isocyanates include compounds classified as potential human carcinogens. Consequently, all stages of the lifecycle of isocyanates are rigorously controlled to minimize emissions, due to concerns over potential risk to human health. Comparing PVC and TPU from environmental point of view, TPU has better environmental protection. TPU is abrasion resistant while PVC can crack over time; it is also more elastic and lighter than PVC. In medical devices it is accepted as a safe alternative to PVC because TPU health-care grades do not contain rubber accelerators and plasticizers [390].

14.3.6.7 3D printing

Flexible filaments are made of TPE, a plastic with rubberlike characteristics. Among several types of TPE, the most commonly used among 3D printing filaments is TPU [393]. TPU offers robust material characteristics that can serve a broad range of functional prototypes where durability and flexibility are important issues [394]. Among flexible 3D printing filaments, TPU is slightly more rigid, making it easier to extrude and use. It is a medium-strength material with very high flexibility and durability, able to withstand much higher compressive and tensile forces than its more common counterparts PLA and ABS [395]. Recommended print settings are presented in Table 14.37.

TPE is softer and trickier to print with, while TPU is firmer and prints more like PETG. In terms of workability, TPU is much easier to handle than TPE. The softness of the TPE filament (shore hardness of only 85A) made it difficult to work with, especially when using a Bowden extruder [396]. To print high-quality objects properly without jamming, a direct drive extruder is recommended [395].

Flexible filaments are not prone to warping during printing, that sway a cooling fan at medium or high setting can be used, which will allow to retain good detail on the print.

TPU may have poor bridging characteristics, leading to prints with multiple blobs and stringing. The right combination of printing temperature, printing speed, and retraction speed is needed to get a good quality printed object [396]. Some tips for printing together with advantages and disadvantages of TPU and TPE are shown in Table 14.38.

TPU does not produce any notable levels of fumes while printing, and is a nonsoluble material, but it is hygroscopic, meaning that it will degrade in wet conditions [395].

Printed objects from TPU cannot be finished to get that polished and smooth look because unlike to PLA or ABS, TPU does not dissolve in chemicals like acetone [396]. Excellent layer to layer adhesion results in good durability of prints.

TABLE 14.37 Print settings for TPU and TPE.

	TPU	TPE
Print temperature (°C)	210–240; 225-245	200–220
Bed temperature (°C)	45–60; 20–70	40–50; 80–100
Print speed (mm/s)	15–30	30–40; 5–30
Bed adhesion	PI tape, blue painter's tape, glue stick, adhesion spray (such as 3DLAC), vinyl hairspray	PI tape, blue painter's tape
Cooling fan	30%–60% after 1st layer, or as needed	
Enclosure (°C)	Not required	Not required

Adapted from Refs. [393,396–399].

TABLE 14.38 Advantages and disadvantages of TPU and TPE.

	TPU
PROS	• Rubberlike elasticity • Good load-bearing capacity • It can bend easily without any effect on the design, strength, and durability • High resilience, good compression set • Resistance to impact, tear, abrasion, scratches, weather • Ability to perform at low temperature
CONS	• Short shelf life • Drying is required before processing • Not as cost-effective as other alternatives • Narrower hardness range • Narrow temperature range for processing • Difficult to print • Poor bridging characteristics • Possibility of blobs and stringing
TIPS	• Printing fast can clog up the extruder: printing speed of 15 mm/s is recommended; up to 30 mm/s is possible depending on the 3D printer model. • The feed rate can be optimized by printing at lower layer heights in the 0.1—0.2 mm range. The lower layer height requires less material, so it allows that extruder operates at a lower feed rate. • Using rafts should be avoided, as the base layers of the raft have higher extrusion rates which may create issues. • When a flexible part needs to fit on top of another object, a negative tolerance between the parts is used, so that the flexible part will need to stretch to fit over the other object snugly.
	TPE
PROS	• High elasticity • Softer than others • Great for impact, or vibration resistance • Nontoxic and safe material • Durable prints • Good choice for antislip objects
CONS	• Difficult to feed into the extruder • Material may buckle when pushed to the extruder • May ooze out while printing, creating messy prints
TIPS	• To feed the filament, a direct path is needed, not to get stuck or deformed. • Buckling is the consequence of the nozzle's pressure — lower print speed is recommended (5 mm/s). • To get good adhesion to the print bed as well as to avoid any shrinkage, the temperature of the print bed must be adjusted. • Stringy or messy prints are the consequence of too much pressure in the extruder. This is connected with the retraction settings, speed, or temperature. If the extruder clogs, the retraction should be lowered. If extra material comes out from the nozzle, retraction speed or distance should be increased.

Adapted from Refs. [390,393,396,399,400].

Typical properties of 3D printing TPU and TPE filaments are presented in Table 14.39. TPU is used to print products that need to bend or flex during application, such as sporting goods, medical devices, footwear, inflatable rafts, outer cases for mobile devices, rubber mats, stress toys, and automotive instrument panels. It has also been used for industry applications due to its resistance to oils, greases, and a variety of solvents. TPU can be used for tires or shock absorbers, and is even occasionally utilized to make o-rings and seals [395]. In Fig. 14.18 TPU 3D-printed outer case for mobile device and TPU printed onto the textile material are shown.

14.4 High-performance polymers

14.4.1 Polyetherimides

14.4.1.1 Development

Polyetherimides (PEIs) are high-performance engineering thermoplastics belonging to group of thermoplastic polyimides (PIs). PI thermoset resins were developed in 1950s and became commercially available around 1963

TABLE 14.39 Properties of 3D printing TPU and TPE filaments.

	TPU	TPE
Density (g/cm^3)	1.22	1.12
Melt flow index (g/10 min)	15.9	
Water absorption: 23°C, 50% RH (%)	0.18	
Tensile strength: Yield (MPa)	8.6	8
Tensile strength: Break (MPa)	39	45
Tensile elongation: Yield (%)	55	
Tensile elongation: Break (%)	580	>400
Tensile modulus (MPa)	26	70
Flexural strength (MPa)	4.3	7
Flexural modulus (MPa)	78.7	65
Notched izod impact (kJ/m^2)	34.4	
Deflection temperature under load: 0.45 MPa (°C)	74	
Vicat softening temperature (°C)	138	111
Melting temperature (°C)	220	147
Surface resistivity (Ohm)	$2\ 10^{14}$	
Volume resistivity (Ohm•cm)	10^{13}	
Dielectric constant	4.12	

Adapted from Refs. [401–403].

[16]. In the late 1980s, Mitsui Chemicals, Inc. developed first thermoplastic PI, a super engineering plastic called Aurum [404]. PEI was first developed in 1982 by General Electric Company under the trade name ULTEM resin, resulted from the research work of J.G. Wirth in the early 1970s [405].

14.4.1.2 Chemical structure and synthesis

Most of the PEIs are made from 4,4′-bisphenol A dianhydride (BPADA), such as tetracarboxylic dianhydride (produced from the reaction of BPA and phthalic anhydride) and a diamine such as m-phenylene diamine (MPD) [406]. IUPAC name is poly(ether imide) and poly(bisphenol A anhydride-*co*-1,3-phenylenediamine). Molecular formula of BPADA–MPD PEI, shown in Fig. 14.19, is $(C_{39}H_{30}O_6N_2)_n$ and molecular weight of repeat unit is 622.66 g/mol [407].

Aromatic PEIs have limited solubility and very high melting point. With incorporation of flexible aryl ether linkages into the PI backbone, processing of PIs can be improved [408]. PEIs are generally prepared by a two-step process from aromatic diamines and aromatic tetracarboxylic dianhydrides (TCDAs). The synthesis proceeds via polycondensation reaction between TCDA and MPD in the case of BPADA-MPD PEI [406]. The reaction that is used for the formation of aromatic ether linkages is the nucleophilic aromatic substitution reaction. This reaction takes place at relatively low temperatures [408]. The key element is the reaction of a diamine and a dianhydride to form an amide-acid polymer via ring opening of the anhydride by nucleophilic attack of the diamine. This is performed at ambient or low temperatures in a high boiling dipolar aprotic solvent. The final step of the process involves the imidization of a diacid anhydride with diamine, such as MPD. PI is formed by removal of water [409,410].

A large variety of PIs can be prepared from a large number of monomers. Several different monomers are used to produce PEI: 4,4′-bisphenol A dianhydride (BPADA), oxydianiline (ODA), pyromellitic dianhydride (PMDA), diamino diphenyl sulfone (DDS), methylene dianiline (MDA), m-phenylene diamine (MPD), p-phenylene diamine (PPD), biphenol diamine (BP diamine). Commercially available PEIs beside BPADA–MPD PEI are biphenol diamine PMDA PEI, BPADA–DDS PEI sulfone, BPADA–PPD PEI, BPADA–PMDA–MPD copolyetherimide [411]. Variations in the structure of the dianhydride and diamine determine the degree of crystallinity, Tg, melting point of PEIs and influence their properties. The condensation products (water or carbon dioxide) and the solvent need to be fully removed prior postprocessing of the resin to achieve high-performance properties [412].

FIGURE 14.18 3D-printed object from TPU and TPU printed on the textile material. *(A) Image credits: AMFG – amfg.ai. (B) Image credits: UL NTF.*

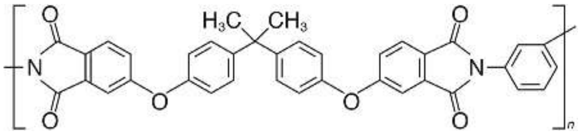


FIGURE 14.19 Repeat unit of PEI (BPADA-MPD).

14.4.1.3 Characteristics

Aromatic PIs exhibit outstanding thermal stability, good chemical resistance, high tensile and impact strength, stiffness, transparency, and excellent electrical properties, which remain stable over a wide range of temperatures and frequencies [408].

PEI has unique combination of high specific strength, rigidity, flexibility, exceptional dimensional strength. A key feature of PEI is maintenance of properties at elevated temperatures. It has good UV-light resistance and weatherability. PEI also displays good hydrolytic stability. Hydrolytic stability tests show that more than 85% of tensile strength is retained after 10,000 h of boiling-water immersion. The material is also suitable for applications requiring

TABLE 14.40 Typical properties of generic PEI polymer.

	PEI
Density (g/cm^3)	1.25–1.37
Melt flow rate (MFR) (g/10 min)	8.1–19
Water absorption: 23°C, 50% RH (%)	0.19–0.7
Water absorption: 24 h, immersed (%)	0.25–0.28
Tensile strength: Yield (MPa)	93.8–111.7
Tensile strength: Break (MPa)	77.2–88.2
Tensile elongation: Yield (%)	6–8.8
Tensile elongation: Break (%)	1.9–80
Tensile modulus (GPa)	2.78–3.51
Flexural strength (MPa)	106.2–161.3
Flexural modulus (GPa)	2.7–3.34
Charpy notched impact strength (kJ/m^2)	2.9–10.9
Notched izod impact (kJ/m^2)	3.8–6.3
Rockwell hardness	109–110
Coefficient of friction	0.23–0.3
Deflection temperature under load: 0.45 MPa (°C)	193–210
Vicat softening temperature (°C)	208–242
Thermal conductivity (W/mK)	0.216–0.259
Surface resistivity (Ohm)	10^2–$4 \cdot 10^{15}$
Volume resistivity (Ohm·cm)	10–10^{17}
Dielectric constant	3.14–3.45

Adapted from Ref. [415].

short-term or repeated steam exposure [413]. It also shows superior electrical properties. PEI resists a broad range of chemicals under varied conditions of stress and temperatures. It is resistant to alcohols, acids, and hydrocarbon solvent but dissolves in partially halogenated solvents. PEI is sterilizable and autoclave resistant [410]. It is inherently flame resistant without the use of additives, with low smoke generation and limiting oxygen index of 47 [406]. The typical service temperature range of PEIs is about −270 to +300°C [412]. PEI is FDA compliant, EU Food Contact Compliant, and ISO10993 compliant in natural color.

PEI is a high-strength amorphous thermoplastic material showing amber transparency, with the characteristics similar to PEEK. Relative to PEEK, it is less temperature resistant, with lower impact strength, prone to stress cracking in chlorinated solvents and less expensive [414]. Typical properties of generic PEI polymer are shown in Table 14.40.

PEI resins are available for general-purpose processing methods as a transparent resin and in standard and custom colors, but also as GF-reinforced grade, bearing grades, and high-temperature grades.

One limitation of PEI is its low colorability, other is stress cracking initiated by the attack of polar chlorinated solvents. PEI is attacked by strong alkalis and partially halogenated solvents. Limitations associated with processing of PEI are need for higher melt temperatures, a long drying before processing and hot mold during injection molding [406]. Because of high cost PEI is applicable only for highly demanding applications.

14.4.1.4 Processing

Thermoplastic PEIs provide unique combination of properties, such as the strength, heat resistance, and flame retardancy of PIs with the ease of melt processing like PC and ABS, although higher melt temperatures are required [416].

The excellent thermal stability is demonstrated by the maintenance of stable melt viscosity after multiple regrinds and remolding. The processing window is nearly 100°C and PEI can be processed by injection molding, blow molding, extrusion, thermoforming, and compression molding on most existing equipment [410]. The excellent flow properties of PEI can be used for the molding of complicated parts and thin sections. PEI is extruded to produce fibers, profiles, coated wire, sheet, and film. Films are made via melt extrusion and solvent casting processes. The polymer can be easily machined with conventional metalworking tools, painted, hot stamped, printed, or metallized [406]. Because of the good thermal stability, its melt temperature is high, 340−440°C. Mostly used processing technique is injection molding.

Processing conditions for injection molding according to Refs. [417,418] are:

- predrying: 140−150°C for 4−6 h,
- mold temperature: 65−180°C,
- melt temperature: 370−400°C,
- material injection pressure: 70−150 MPa.

14.4.1.5 *Applications*

PEIs are used for demanding applications in aerospace, automotive, and transportation. PEI is suitable for use in internal components of microwave ovens, electrical and electronic products, and appliance [410]. Some other important applications include probe housing, digital card printer frames, coil springs, and cable guards [412].

Flame resistance, coupled with high strength, dimensional stability, and excellent electrical properties, enables use in all sorts of electrical applications: circuit boards, burn-in sockets, switches, connectors, kitchen appliance components, high-temperature lighting, insulating tapes, and dielectric films. Long-term-creep resistance, high strength retention at elevated temperatures, coupled with good chemical resistance, enables use in under-the-hood automotive applications [419]. Creep resistance over the long term allows PEI to replace metal and other materials in many structural applications. Electrical properties show excellent stability under variable temperature, humidity, and frequency conditions [420]. PEI is also used in packaging applications, medical/health-care applications due to its heat and radiation resistance, hydrolytic stability, and transparency [417]. Laboratory ware and health-care applications rely on PEI for its resistance to chemicals and gamma radiation sterilization. High-strength fibers are used for industrial filters, papermaking drying screens, and flame-resistant garment fabric for firemen and race car drivers. Fiber optics is another growing market [419], as well as 3D-printed products.

14.4.1.6 *Recycling*

Recycling helps reduce material costs and recover value. PEI is advance engineering material and is not collected and recycled in most of commercial recycling plants. PEI waste, as other plastic, can be damaging to the environment. 3D misprints must be separated with plastic waste together with the filament reel.

There are some specialized companies that can recycle PEI. During the PEI recycling processes, nothing is added. By plant scrap recycling or decontamination and cleaning high value plant scrap is converted into clean, cost-saving raw materials. Custom configured processing removes dust, fines, debris, and foreign material contamination [421]. In the study of Bastida et al. [422] the effect of reprocessing by successive injection molding at 330°C and regrinding up to 5 times on properties of PEI was studied. It was established that degradation took place in first two cycles, but in next cycles molecular weight of PEI did not change and the deterioration of mechanical properties was quite low.

14.4.1.7 *3D printing*

PEI is an advanced material with the highest thermal resistance in the market, having a Tg of 215°C and a maximum working temperature of 200°C. The main advantage, compared to other materials, is its great dimensional stability and stability of mechanical properties [423]. The high strength, rigidity, melt temperature, and thermal stability of PEI make this material unique, though quite demanding for 3D printing [424]. At first, the only company capable of 3D printing with the material was Stratasys; today several other companies have produced printers capable of handling PEI or PEEK.

Recommended 3D printing conditions according to Refs. [423,425] are:

- print temperature: 350−380°C; 370−400°C,
- bed temperature: 140−160°C,
- print speed: 1000 mm/min, 40−100 mm/s,
- bed adhesion: PEI tape, PI tape, PVP glue stick, lightly sanded glass-reinforced epoxy laminate (FR4), or perfboard,
- cooling fan: none,
- enclosure: heated required.

TABLE 14.41 Advantages and disadvantages of PEI.

	PEI
PROS	• Exceptional mechanical properties • The highest tensile strength among of all FDM filaments • Excellent thermal and dimensional stability • Continuous use temperature of 180°C • Resistant to flame, chemicals, hot water, and steam • Excellent machinability and finishing characteristic
CONS	• High processing temperatures required • Only a few 3D printers capable of handling the material • Very expensive • No color choices (amber or sometimes transparent), translucent and opaque-clear is not available
TIPS	• Drying before printing at 140–150°C for 4–6 h for a maximum moisture content of 0.01%–0.02% is needed. • Residual moisture of filaments must be below 0.02% to prevent foamy extrusion due to high vapor pressure caused by trace of moisture at high printing temperatures. • Preheating the build plate and chamber temperatures to 160°C and 90°C, respectively, for at least 30 min before printing is needed. • The print chamber must be kept at an evenly distributed high temperature because cold areas can cause unevenly shrinking. This can result in warping and lack of bonding of layers. • Printed object must be removed from the build plate while its temperature is still high, to avoid breakage of glass plate, because the print may shrink more rapidly than the glass plate. • Annealing the printed object in a hot-air oven reduces any printed-in stresses present.

Adapted from Refs. [424,425,427–429].

PEI has an excellent adhesion between layers which results in great improvement of the impact resistance, strength, durability, and the printing process [426]. PEI stands out in mechanical properties; for example, elastic and flexing moduli surpass all conventional and technical 3D printing materials, such as PA-carbon, PC, ABS, etc. [423]. PEI is a more affordable alternative to PEEK, but has a lower impact strength and useable temperature.

With a melting temperature between 345 and 400°C the engineering challenge is maintaining high temperature in the chamber and has it evenly distributed. Managing the temperature in the printhead and in the printed object layers to get them solid is the biggest challenge, especially to print objects with substantial volume and get a high resolution. Any cool areas cause that PEI shrinks unevenly. This can result in warping and even a lack of bonding to the previous layers. An issue with 3D printing at such high temperatures is also the potential damage that can be done to the components within the machine [427]. Some tips for 3D printing are given in Table 14.41, together with advantages and disadvantages of PEI.

Typical properties of 3D printing PEI filament are given in Table 14.42 and in Fig. 14.20 3D print from PEI is shown. The printed object maintains the structural shape even at raised temperature. The short cycle injection molding tools, CF lamination tools, and other types of molds that are subject to high pressure and temperature are some of 3D-printed applications [423]. PEI is fireproof material, with good chemical resistance to halogen hydrocarbons, automotive fluids, alcohol, and aqueous solutions. This, together with its low density, makes the PEI applicable in the field of aeronautics, transportation and the automotive industry [423]. PEI is used to create functional prototypes and production parts for high-strength, FST-rated, and certified applications using 3D printing (Fig. 14.20) [406]. Thanks to its high strength and thermal stability, it can be used in out-of-cabin aerospace applications (ducts, clips, semistructural components) as well as automotive applications. Its food-contact and biocompatibility certifications mean that PEI is a great option for applications such as food production tools and custom medical devices [430]. Its high dielectric stability (resistance to transforming an electrically insulating material into conductive) and a large capacity of heat dissipation makes it an excellent material for manufacturing of insulating parts for electronic circuits or housings for electrical outlets [423]. PEI is a reusable, relatively maintenance free build surface for both ABS and PLA requiring no additional adhesives such as glue or tape [431]. It can be used for all types of filament on a heated or unheated print bed [432].

14.4.2 Polyaryletherketones

14.4.2.1 Development

Polyether ether ketone (PEEK) is the most known aromatic organic thermoplastic polymer in the polyaryletherketone (PAEK) family. The PAEK family brings together polymers with a linear chain composed of alternating aromatic rings and ketone or ether groups [434]. They belong to the high-performance polymers.

TABLE 14.42 Properties of 3D printing PEI filament.

	PEI
Density (g/cm^3)	1.27
Melt flow index (g/10 min)	13–25
Water absorption: 23°C, 50% RH (%)	0.7
Tensile strength: Yield (MPa)	105
Tensile strength: Break (MPa)	85
Tensile elongation: Yield (%)	6
Tensile elongation: Break (%)	60
Tensile modulus (GPa)	3.2
Flexural strength (MPa)	160
Flexural modulus (GPa)	3.3
Notched izod impact (kJ/m^2)	5
Deflection temperature under load: 0.45 MPa (ºC)	200
Vicat softening temperature (ºC)	215
Melting temperature (ºC)	340
Thermal conductivity (W/mK)	0.21
Volume resistivity (Ohm•cm)	10^{15}–10^{17}
Dielectric constant	3.15

Adapted from Refs. [423,426,433].

FIGURE 14.20 3D-printed object from PEI. *Image credits: 3DGence.*

The original invention of PEEK and patent holds Victrex PLC. Imperial Chemical Industries ICI has developed and commercialized it in 1978 [435]. The industrial production started in 1987, in which the preparation for PEEK was carried out through solution polycondensation reaction with diphenyl sulfone as the solvent in a salt-mixed system of K_2CO_3/Na_2CO_3 and with 4,4′-difluorobenzophenone (or 4,4′-dichlorobenzophenone) and hydroquinone as raw materials [435].

Polyether ketone ketone (PEKK) was invented in the 1960s as part of the Apollo space program [436]. It was the first PAEK family member to be introduced in 1962 [437]. The processing of PEKK was originally developed by Dupont [438]. As commercial production requires an expensive, complex process it was commercialized quite late. Demand for PEKK has been driven by the need for lighter materials in rigorous applications like aerospace and offshore oil extraction [436]. Oxford Performance Materials has been working with PEKK since 2000, developing both material and applications technology. In 2011, company Arkema started industrial PEKK production.

14.4.2.2 Chemical structure and synthesis

Polyarylketones are typically produced by the reaction of an aromatic dihalide (chloride or fluoride) with a diphenol [357]. Structurally, PEEK is a polymer formed by the connection of ether bonds, ketone groups, and aromatic rings, prepared through polycondensation of dihydroxy phenol (disodium 1,4-benzenediolate) and 4,4′-difluorobenzophenone. The IUPAC name is poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene). Molecular formula is $(C_{19}H_{12}O_3)_n$ and the molecular weight is 288.30 g/mol [439].

PEKK is prepared by combining diphenyl ether and a terephthaloyl halide, such as terephthaloyl chloride. The IUPAC name is poly(1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylenecarbonyl), and the molecular weight of repeat unit is 300.3 g/mol [440]. The chemical formula is $(C_{20}H_{12}O_3)_n$. In Fig. 14.21 chemical structures of VESTAKEEP, Zeniva, Victrex type of PEEK and of Kepstan, Cypec type of PEKK are shown.

PEEK polymers are obtained by step-growth polymerization by the dialkylation of bisphenolate salts [441]. The chemical formula of PEEK is $(O{-}R{-}O{-}Ph{-}(C{=}O){-}Ph)_n$, wherein the R group can be benzene, biphenyl, or terphenyl, and therefore the preparation for PEEK can be carried out with hydroquinone, diphenol, and diphenol triphenyl as initiators [442]. The polymers may be made by condensation of hydroquinone, 4,4′-dihydroxydiphenyl and 4,4′-difluorobenzophenone in the presence of an alkali metal carbonate or bicarbonate and of an aromatic sulfone solvent, e.g., diphenyl sulfone [443].

PEEKs are made by either nucleophilic or electrophilic process. In the nucleophilic route a high boiling solvent diphenyl sulfone is used. In this reaction hydroquinone is transformed into its di-potassium salt by heating with an equivalent amount of potassium carbonate or potassium bicarbonate, with simultaneous removal of the water at 150−200°C, followed by addition of the second monomer, namely, 4,4′-difluorobenzophenone. The polymerization reaction is carried out at 320−350°C [444]. A second method is by the Friedel−Crafts acylation method using a catalyst like boron trifluoride. The solvent is hydrofluoric acid and the reaction is conducted at room temperature. The polymer formed remains in solution till it is precipitated, purified, and dried [357]. In electrophilic process Friedel−Crafts catalysts, $AlCl_3$ is used for the polymerization of a carboxylic acid chloride derivative of phenoxy benzoic acid (PBA) and phenoxy phenoxy benzoic acid (PPBA) [445]. The preparation process of PEEK under a low temperature of 40−160°C with phenoxyl-phenoxy benzoic acid as the only monomer and alkyl sulfonic acid as the solvent is also possible. A melt processible PEEK polymer synthesized electrophilically using methane sulfonic acid containing methane sulfonic anhydride or phosphorous pentoxide is described in the patent US6566484B2 [444].

PEKK can be obtained in amorphous or semicrystalline form, with different para/meta phenyl isomer ratios from diphenyl ether, terephthaloyl, and isophthaloyl chloride. The polyetherketoneketone has repeating units represented by formula I and formula II: $-A-C(=O)-B-C(=O)-$ (I) and $-A-C(=O)-D-C(=O)-$ (II) where A is a $-Ph-O-Ph-$ group, Ph is a phenylene radical, B is p-phenylene, and D is m-phenylene [446].

PEKK may be formed using an electrophilic polymerization by the Friedel−Crafts method. In the original process invented by E.G. Brugel (DuPont) polymerization is completed at high temperatures. Following catalyst addition to the diphenyl ether and the acid chloride in solvent the temperature of the reaction mixture is increased to about 100°C [438].

PEKK polymers are made from a tailored combination of two monomers (terephthaloyl and isophthaloyl). The formulations are expressed by the ratio of terephthaloyl (T) to isophthaloyl (I) moieties used during the synthesis. The T/I ratio affects PEKK Tg, Tm, and crystallization kinetics [447,448]. Tailored molecular weight control leads to

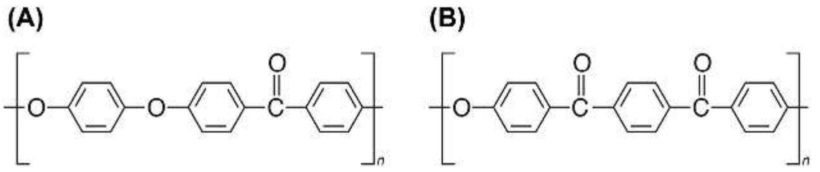


FIGURE 14.21 Repeat units of: (A) PEEK, (B) PEKK.

grades with highly specific melt volume indexes (from highly fluid to highly viscous). The crystallinity of PEKK depends on the thermal history and processing conditions. When quenching is applied, PEKK is in the quasi-amorphous state whereas a semicrystalline PEKK can be obtained with slow cooling conditions or by isothermal crystallization between Tg and Tm [434].

Solvay and Arkema practice the DuPont method, which uses high-temperature synthesis. Recently, low-temperature synthesis was developed in order to produce polymer which is also much more controllable in terms of the finished polymer's molecular weight and molecular structure [449].

14.4.2.3 Characteristics

PEEK is a high-performance semicrystalline, nonhomogeneous thermoplastic material. The aromatic rings provide stiffness, heat, and radiation resistance, whether the ether and ketone links provide flexibility and thermal processability to these very high-temperature ketones [357]. Its mechanical and physical properties are very good. This material is tough, strong, and rigid and has superior creep resistance, and one of the highest strength-to-weight ratios available among polymers [450]. It provides an excellent balance of properties where the material is required to withstand high loadings for long periods at high temperature without permanent deformations [441].

The melting point of PEEK is above 330°C, the load thermal deformation temperature is as high as 315°C, and the continuous use temperature is up to 260°C [442]. PEEK has very high temperature resistance, chemical resistance, and exceptional dimensional stability. It is chemically inert, resists radiation and a wide range of solvents, and has inherently low flammability and smoke emission [357]. With its resistance to hydrolysis, PEEK can withstand boiling water and superheated steam used with autoclave and sterilization equipment [451]. However, at temperature higher than 200°C, resistance to chlorine/bromide, fluorine, HF and HBr, concentrated sulfur and nitric acids, ketones, and nitrobenzene is low [452]. PEEK also has very good resistance to wear, abrasion, and dynamic fatigue, combined with a low coefficient of friction [414]. The polymer exhibits high volume resistivity and surface resistivity. It can maintain good insulating properties in a broad temperature range and environmental changes [441]. Typical properties of generic PEEK polymer are shown in Table 14.43.

PEEK is pale amber in color. Thicker samples are usually semicrystalline and opaque, whereas thin films are usually amorphous and transparent, though still amber in color [414].

PEEK shows in comparison to:

- fluoropolymers, higher tensile strength, higher deflection and operating temperature, bonding, better processing, and toxic gas emission; but is inferior in terms of chemical resistance, cost, toughness, and UV weathering [441];
- PPSU superior thermal resistance, toughness, and flashing [441];
- PES much higher temperature performance, wear resistance, chemicals resistance, and fatigue performance [441];
- PEI lower Tg, tensile strength, LOI, and moisture absorptivity. PEI has better overall properties and performance, except hydrolytic stability, which is better at PEEK [435].

The main limitations of PEEK are low resistance to UV light and lower stability in halogens, concentrated sulfuric, nitric, and chromic acids. It needs to be processed at high temperatures and because it is expensive it is mainly applicable for highly demanding applications [441].

PEEK forms miscible blends with a range of other polyketones and PEI. With the incorporation of fillers and reinforcements like glass and carbon fibers, the mechanical properties of these materials can be tailored to a wide range of performance requirements and applications [357]. When reinforced with CFs, tensile strength of 200 MPa can be achieved with excellent properties retained at 299°C. Its flexural modulus at very high temperatures can further be improved with glass or carbon reinforcement [441].

PEKK has the characteristics common to PAEK group of high-performance thermoplastics. It is strong, stiff, hard, with high temperature resistance, good chemical resistance, and inherently low flammability and smoke emission [457]. It has outstanding temperature performance, continuous use temperature 250−260°C, and short-term exposure up to 300°C. It is resistant to most of organic and inorganic chemicals (sensitive to very aggressive reagents like fuming sulfuric and nitric acid, methylene chloride). It also has very good resistance to wear, dynamic fatigue and radiation, excellent barrier properties (CO_2, H_2S, etc.), but it is difficult to process and very expensive [458].

The ratio and sequence of ethers to ketones affect the thermal properties including Tg, melting point, heat resistance, and processing temperature of the polymer. As PEKK has a higher ratio of ketones than PEEK and the polymer chain is more rigid the Tg (162°C) and the melting point of PEKK ($Tm = 395°C$) are higher than the ones of PEEK ($Tg = 143°C$, $Tm = 343°C$) [357,440,457].

TABLE 14.43 Typical properties of generic PEEK and PEKK polymers.

	PEEK	PEKK
Density (g/cm^3)	1.3	1.28–1.31
Melt flow rate (MFR) (g/10 min)	1.6–36	30–120
Water absorption: 23°C, 50% RH (%)	0.12–0.2	0.2
Water absorption: 24 h, immersed (%)	0.088–0.5	0.2–0.5
Tensile strength: Yield (MPa)	72.4–112.4	88–112
Tensile strength: Break (MPa)	68.7–75.2	90–110
Tensile elongation: Yield (%)	4.7–5.1	5.2–5.4
Tensile elongation: Break (%)	1.6–41	12–80
Tensile modulus (GPa)	2.07–5.69	3.4–4.4
Flexural strength (MPa)	99.3–182	128–190
Flexural modulus (GPa)	2.74–4.56	3.4–4.6
Charpy notched impact strength (kJ/m^2)	3.4–8	4–5.5
Notched izod impact (kJ/m^2)	4.4–9	
Rockwell hardness	89–106	86–88
Coefficient of friction	0.2–0.53	0.26–0.29
Deflection temperature under load: 0.45 MPa (°C)	201.5–210	141–175
Vicat softening temperature (°C)	304–335	
Melting temperature (°C)	340–343	306–360
Thermal conductivity (W/mK)	0.245–0.317	0.25
Surface resistivity (Ohm)	10^4–10^{18}	
Volume resistivity (Ohm•cm)	10^6–$1.2 \cdot 10^{17}$	10^{16}
Dielectric constant	2.85–3.52	2.5–3.3

Adapted from Refs. [453–456].

Compared to PEEK, PEKK generally offers higher temperature performance (higher Tg and Tm), significantly higher compression strength, better impact resistance, a broader range of tailored properties, improved barrier performance, better wetting and adhesion, and better coefficient of friction control [458,459].

14.4.2.4 Processing

Although processing of PEEK is intricate because of the high processing temperature and inertness to most of the solvents, it can be processed by conventional sintering and hot melting processes or by using powder prepreg methods [460]. However, PEEK has good processing performance, and can be processed by conventional methods such as injection molding, compression molding, and extrusion into shapes, film or filaments, thermoforming, spray coating, or stock shape machining [461]. PEEK is suitable for injection of very small parts with tight dimensional tolerances.

Though PEEK is a very popular engineered plastic for injection molding, it can also be difficult to work with. Because it must be heated to very high temperatures, melt temperature is 370–420°C and mold temperature is 180–210°C, a special equipment is required. PEEK is also sensitive to anisotropic shrinking during the cooling process and requires the right amount of pressure to the mold to maintain product integrity [462,463].

PEEK extrusion can proceed with the most standard screw machines, provided that they can operate reliably at the required processing temperatures. The optimum processing temperatures of PEEK depend on the viscosity of the compound and the technical parameters of the extrusion unit [463]. PEEK is sensitive to heat; a good heat profile in the extruder barrel is required to maintain dimensional stability of the extruded part. Cooling can be done using water, oil, or air. A quickly cooling results in amorphous structure and imparts a transparent amber color, whereas slowly cooling leads to crystal form for a tan opaque finish [464].

The material has a semicrystalline structure but can be extruded to maintain amorphous qualities or to a very hard finish. Cooling temperature has a strong influence on crystallinity and then on performances. For film and sheet extrusion, cooling cylinders at 50°C lead to transparent amorphous material, whereas temperature of 170°C leads to opaque and highly crystalline material [441].

Recommended processing conditions for extrusion according to Refs. [463,465] are:

- predrying: 8−12 h at 170°C,
- melt temperature: 343−400°C,
- screw design (L/D ratio): 18:1 to 24:1.

PEKK is unique among the other PAEKs because it has the ability to synthesize isomeric copolymers to affect the Tm and significantly widen the melt processing window [448]. These enable lower processing temperatures and the ability to process PEKK copolymers as either amorphous or semicrystalline structures, depending on processing technologies and cooling conditions. It can be injection molded and extruded as an amorphous polymer without the need for quenching [466].

PEKK has an extremely slow rate of crystallization leading to improved flow characteristics, lower mold-in stresses, and greater dimensional stability. PEKK also exhibits lower melt viscosity than PEEK, rendering easier processing of injection molded products [457].

PEKK can be processed by injection molding, extrusion and compression molding, thermoforming, laser sintering, powder coating, and 3D printing. Compared to PEEK melt and mold temperatures are higher up to 10°C [467].

14.4.2.5 Applications

PEEK polymer provides exceptional performance over a wide range of temperatures and extreme conditions. It is excellent for applications where thermal, chemical, and combustion properties are critical to performance [451]. Many performances such as resisting abrasion, chemicals, fire, hydrolysis, radiation, and the like qualify this polymer to be used in military, aviation, automobile manufacturing, electronic apparatus, medical treatment, food, etc. [442]. It is extensively used in the aerospace, automotive, and chemical process industries [468]. PEEK is ideal for exterior aerospace conditions where the material comes into contact with atmospheric particles and low temperatures [468].

Its exceptional mechanical properties with resistance to heat, chemicals, wear, fatigue, and creep enable its use as a replacement for metals in a wide variety of high-performance end-use applications, such as components for cars, aircraft, industrial pumps, valves and seals, connectors, and instruments [469]. The main benefits of replacing metals with PEEK are besides weight reduction, enhanced performance, and greater design freedom. Greater design freedom allows complex geometries to be molded-in without labor-intensive postmachining steps [461].

PEEK has excellent electrical properties and provides parts with long-term operating reliability over widely fluctuating ranges of temperature, pressure, and frequency, which is important in electrical/electronic applications. Applications are in the chemical process industry (compressor plates, valve seats, pump impellers, thrust washers, bearing cages), aerospace (aircraft fairings, radomes, fuel valves, ducting), and electrical (wire coating, semiconductor wafer carriers) industries [410]. FDA-approved PEEK finds its application in food processing industry mainly as a bearing and seals for food processing equipment [470]. PEEK fabrics are used for high temperature (over 150°C) drying of food and feed, filters and membranes are applied in chemical and pharmaceutical process industries [468]. Medical applications include surgical instruments and tools, sterilization equipment, and dialysis machine components. For medical instruments that are repeatedly sterilized, the polymer's ability to withstand heat, chemicals, and radiation is important. Trauma, orthopedic, and spinal implants take advantage of its stiffness, strength, wear resistance, and biocompatibility of PEEK [357].

PEKK is often used in extreme operating environments because the material exhibits superior ablative characteristics that include flame and ultraviolet radiation retardancy, superior chemical resistance, excellent heat release, extremely low outgassing, and toxicity [471]. Because of PEKK's excellent mechanical properties, including high stiffness, high toughness, and long-term creep and fatigue resistance, mechanical parts made of (fiber-reinforced) PEKK can replace steel in many applications. It is widely used in the aerospace, automotive, and chemical industries for various structural components [472]. A high dielectric stability and a large capacity of heat dissipation and frequency make it ideal for manufacture insulating parts for electronic circuits or housings for electrical outlets [473]. Both, PEEK and PEKK are increasingly used in AM market.

14.4.2.6 Recycling

PEEK is fully recyclable, either mechanically or as feedstock. Recycled PEEK can be in the form of powder, regrind, flake, and pelletized products. PEEK is manufactured and used in low tonnages, but is very expensive, thus making recycling a necessity [474]. PEEK leftovers can be remolded and reshaped. Company Power Plastic Recycling is involved with PEEK recycling from collected scrap of PEEK Plastic [475]. Company Minger produces PEEK-recycled material from clean and single-origin industrial wastes [476]. Further research is ongoing and PEEK is not being recycled extensively at present.

PEEK and PEKK are manufactured and used in low tonnages, are halogen free, and RoHS compliant. On overheating and combustion of PEEK, carbon monoxide and carbon dioxide are formed. Formation of other hazardous decomposition depends upon the fire conditions. In many cases, recycling is not feasible, hence waste disposal of PEEK products should be by incineration or landfill. The PEEK waste is not biodegradable. Toxicity of PEEK is expected to be low based on insolubility of polymer in water [474].

14.4.2.7 3D printing

The PAEK family of thermoplastics exhibits exceptional thermal, chemical, and mechanical properties. PEKK stands out when considering high values of deformation resistance. 3D printing of PEEK allows construction of almost any complex design geometry. PEEK 3D printing filament has a wide range of unique qualities. Also, its low moisture absorption is one of the advantages of this material [441]. The material has an excellent adhesion between layers which results in good impact resistance, strength, and durability [477]. PEKK is a 3D-printed variant similar to PEEK material, operating in much the same way as PEEK (Fig. 14.22) [478]. Compared to PEEK, PEKK offers enhanced interlayer adhesion, better visual appearance, better crystallization, and slower crystallization speed and can be printed at lower temperature [479]. Recommended print settings for PEEK and PEKK are shown in Table 14.44.

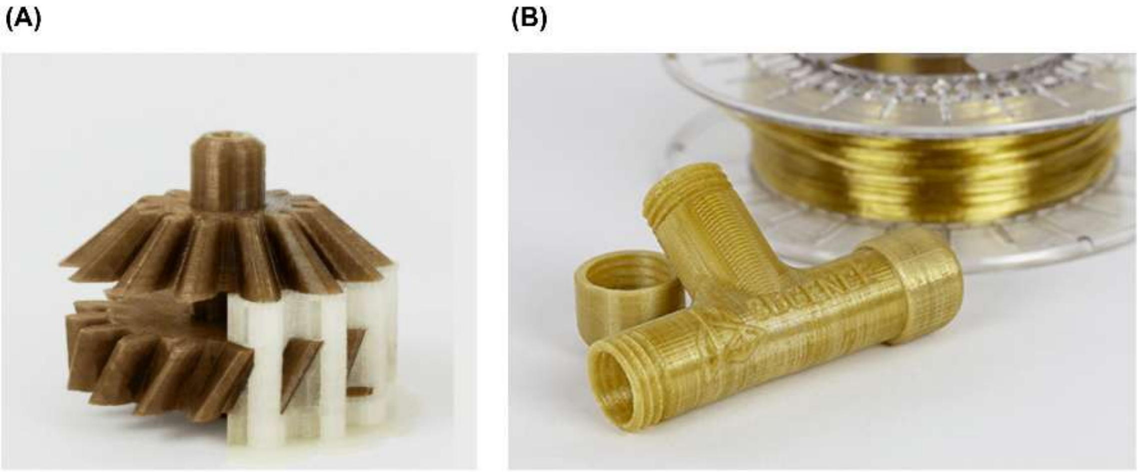


FIGURE 14.22 3D-printed objects from (A) PEEK and (B) PEKK. *Image credits: 3DGence.*

TABLE 14.44 Print settings for PEEK and PEKK.

	PEEK	PEKK
Print temperature (°C)	370–450; 375–410	345–375; 355–385; 360–400
Bed temperature (°C)	120–150; 130–145	120–140
Print speed (mm/s)	10–50; 10–40	20–50; 20–40
Bed adhesion	PEI sheet, glue stick on clean glass, PI tape	PEI sheet, glue stick on clean glass, PI tape
Enclosure (°C)	70–150	70–150; 70–140

Adapted from Refs. [430,452,480,481].

The main disadvantage is quite high price for PEEK 3D printing and need for a well-performing high-temperature 3D printer to get the expected result. Prior to printing, it is necessary to keep residual moisture of filaments below 0.02% to prevent foamy extrudate due to high vapor pressure caused by trace of moisture at high printing temperature. Similar as PEI, PEEK also needs preheating of the build plate and closed build chamber for optimal results [429]. PEEK is sensitive to the fluctuation in temperature that can result in PEEK beginning to speck or in improper crystallization [452]. Crystallization issues, misprints, and deformation occur often because of temperature control issues [482].

Different colors within the printed object, a brown discoloration as opposed to a beige color, mean that the temperature was not controlled sufficiently during the 3D printing process [452]. Printed parts must be annealed after printing to relax stresses and to improve mechanical, thermal, and chemical resistance properties.

Advantages and disadvantages of PEEK and PEKK are presented in Table 14.45. In Table 14.45 also some tips for printing are given.

TABLE 14.45 Advantages and disadvantages of PEEK and PEKK.

	PEEK
PROS	• Outstanding mechanical, thermal, and chemical resistance • Very high strength to weight ratio • Excellent fatigue and chemical resistance properties • Low moisture absorption • Continuous use temperature of 260°C, higher for short duration • Enhanced performance • No biocompatibility concerns • Low release of harmful fumes
CONS	• Very expensive filament • Only few compatible FDM printers on the market • High cost of printed components • Z-strength is a serious issue • Can be challenging to print
TIPS	• 3D printer with adequate thermal manage and closed build chamber to avoid misprints and deformation is required. • Difference in temperatures in different parts of the printer or nozzle assembly leads to specking. • It is vital to keep the filaments away from moisture before and during printing; predrying (150°C/3 h). • 30 min before printing the build plate and chamber are heated at 160°C and 90°C, respectively. • Lower printing speed leads to more accurate printed object. • To avoid different colors of different layers (brown surface discoloration (improper crystallization)) the temperature must be controlled throughout the print; raising the temperature could solve this. • Annealing: 100°C (1 h), 150°C (1–3 h) and 100°C (30 min) or 150°C (1 h), 200°C (1 h) and 150°C (30 min).
	PEKK
PROS	• Among the most powerful materials within 3D printing • Great strength, toughness, and wear-resistance • Superior ablative characteristics • Superior chemical resistance • Extremely low outgassing and toxicity • High dielectric stability, large capacity of heat dissipation • Easier to 3D print than PEEK
CONS	• Very expensive filament • Only few compatible FDM printers on the market • High cost of printed components • Anisotropic • Not resistant to nitric acid, sulfuric acid, or methylene chloride • A lot of experience in 3D printing is needed
TIPS	• If the nozzle temperature is too high, it can result in part deformation and filament oozing. If it is too low, the interlayer welding is weakened along with poor printing of fine features due to the increased polymer viscosity. • If the bed is too cold, the first layer may not attach strongly, and the part may warp or even shift in the middle of a print run.

Adapted from Refs. [429,452,471,473,480,482,483].

TABLE 14.46 Properties of 3D printing PEEK and PEKK filaments.

	PEEK	PEKK
Density (g/cm^3)	1.3–1.31	1.29
Water absorption: 23°C, 50% RH (%)	<0.1	0.16
Tensile strength: Yield (MPa)	85–105	93
Tensile strength: Break (MPa)	48–97	80–100
Tensile elongation: Yield (%)	4.8	4.3
Tensile elongation: Break (%)	5–30	6–10
Tensile modulus (GPa)	3.1–3.8	3.1–3.9
Flexural strength (MPa)	130–145	142
Flexural modulus (GPa)	3.4–3.9	3.1
Charpy notched impact strength (kJ/m^2)	4.2	
Notched izod impact (kJ/m^2)	5	
Deflection temperature under load: 0.45 MPa (°C)	145–156	150
Melting temperature (°C)	343	334
Thermal conductivity (W/mK)	0.32	
Surface resistivity (Ohm)	$>10^{12}$	$>10^{16}$
Dielectric constant	3.2	3.23

Adapted from Refs. [487–492].

Main applications of PEEK in AM include metal-replacement, functional prototyping, and end-use parts for industries like aerospace, automotive, oil and gas, medical, dental, and research [471]. In medical applications, PEEK can replace titanium and ceramic implants, especially as customized implants to solve difficult medical problems [484].

Thanks to its unique mechanical, physical, and chemical properties, PEKK lends itself to a broader range of uses than PEEK. Its chemical resistance means it can be used for components exposed to hydrocarbons, such as fuels and lubricants, as well as many acids. Additionally, low outgassing allows PEKK to be used in confined spaces and sensitive environments. A high operating temperature makes it viable for production of components under the hood or in engine compartments [478]. Best fit applications are high value production parts, manufacturing aids, and prototypes being able to functional testing of parts. PEKK is used in low volume demand; typical use cases are customized parts [485].

Enhanced performance benefits of PEEK and PEKK compared to metals include extending lifetime by eliminating corrosion, increasing fuel efficiency with lower friction, and handling higher loads/speeds to operating in more extreme chemical environments [486]. In Table 14.46 typical properties of PEEK and PEKK filaments are presented.

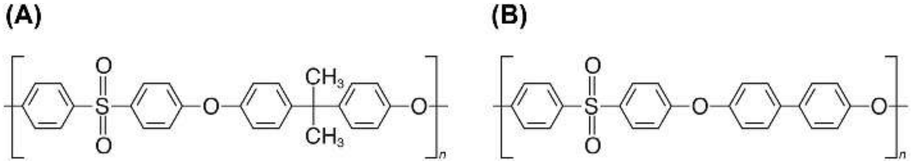
14.4.3 Polyphenylsulfones

14.4.3.1 Development

Polyarylethersulfones (PAESs), also known as sulfone polymers or simply polysulfones (PSUs), have an aromatic backbone structure comprised of phenyl rings, sulfone groups, and ether linkages. They are a subclass of the larger family of high-performance polymers known as polyarylethers that includes polyarylethersulfones (PAESs), polyaryletherketones (PAEKs), and polyaryletherimides (PAEIs) [493].

The first successful reaction yielding useful molecular weight PSU was prepared by R. N. Johnson in 1961. He used the addition of potassium t-butoxide to a dimethyl sulfoxide solution of bisphenol A and dichlorodiphenylsulfone. Additionally, they improved the process by the use of alkali metal hydroxides (first potassium, then sodium) to form the bisphenol salt in situ before the sulfone was added [494]. The first of the sulfone polymers was introduced commercially by Union Carbide Corp. in 1965 as Udel Polysulfone [493]. Polyphenylsulfone (PPSU) was first

FIGURE 14.23 Repeat units of: (A) PSU, (B) PPSU.



introduced commercially by Union Carbide in 1977, and industrial commercialized in 1990 by Amoco Corporation as Radel R PPSU [495].

14.4.3.2 Chemical structure and synthesis

PSUs are prepared by a polycondensation reaction of the sodium salt of an aromatic diphenol and bis(4-chlorophenyl)sulfone. PSU is produced by the reaction of a bisphenol A and bis(4-chlorophenyl)sulfone. The structure-based name is poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(dimethylmethylene)-1,4-phenylene] [171]. The chemical formula and molecular weight of repeat unit are $(C_{27}H_{22}O_4S)_n$ and 442.52 g/mol [496].

Polyphenylsulfone (PPSU, PPSF) is made from 4,4′-dichlorodiphenylsulfone and 4,4′-biphenol. The IUPAC name is poly(oxy-1,4-biphenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene), the chemical formula is $(C_{24}H_{16}O_4S)_n$, and the molecular weight of repeat unit is 400.45 g/mol [497]. Repeat units of PSU and PPSU are shown in Fig. 14.23.

The synthesis of PSUs can proceed by the aromatic nucleophilic substitution or by electrophilic Friedel−Crafts synthesis. The most important method is polycondensation reaction, the aromatic nucleophilic substitution. This process involves reacting equimolar amounts of 4,4′-dihalodiphenylsulfone, such as 4,4′-dichlorodiphenylsulfone, with the appropriate bisphenol. In the case of PSU bis(4-hydroxyphenyl)-2,2-propane is used, while PPSU is made with 4,4′-dihydroxydiphenyl [495]. In a two-step process, first a sodium hydroxide is used for the in situ conversion of bisphenol to disodium salt of this bisphenol. The reaction is carried out in a polar aprotic solvent. With the use of alkali metal carbonate, such as sodium carbonate in a dipolar aprotic solvent, no separate step for the formation of dialkali metal salt of bisphenol is needed [495].

14.4.3.3 Characteristics

PSU together with PEI and HT-PC (high temperature PC) form the largest group of amorphous high-temperature polymers [498].

PSUs are amber-to-yellow transparent engineering resins. They have high strength, stiffness, toughness, and substantial energy absorption capacity. Mechanical properties are kept over a wide temperature range, extending from −50°C to values near the Tg (187°C (PSU), 220°C (PPSU)). The key features of PSUs are short-term temperature resistance up to 220°C, long-term service temperatures up to 180°C, dimensional stability, and creep strength at high temperatures. They also show resistance to hot water and coolants, as well as to fuel and fluorine and oil resistance even at temperatures up to 170°C [499]. PSU polymers are inherently flame retardant, with high resistance to thermal aging, and provide excellent thermal stability in air. They possess good electrical properties that stay unchanged over a wide range of temperatures and frequencies [500].

Thermal degradation of PSU begins at temperatures above 400°C. Products made of PSU are characterized by low flammability, low flame propagation, and especially low smoke emission. They are resistant to high-energy radiation (beta, gamma, X-rays) over the entire range of working temperatures. PSU has an exceptionally high heat-deflection temperature, excellent thermal stability and is recommended for applications where low-temperature toughness is required [501].

PPSU is known for its high toughness, high flexural and tensile strength, impact strength to 200°C, excellent hydrolytic stability, and good resistance to chemicals and heat [502]. This polymer also offers high deflection temperatures and outstanding resistance to environmental stress cracking [500]. Compared to PSU, PPSU has superior mechanical properties and the best chemical resistance of all PAESs. It is highly resistant to mineral acids, bases, salt solutions, oxidizing agents, and most solvents. However, aromatic solvents and oxygenated solvents, such as ketones and ethers, might cause some stress cracking [502]. Typical properties of generic PSU and PPSU polymers are presented in Table 14.47.

PSU and PPSU can be repeatedly sterilized in superheated steam and largely retain both their transparency and their high level of mechanical properties. Especially PPSU performs extremely well; even 2000 superheated-steam sterilization cycles under load are possible without any crack formation [499]. PSUs are ISO10993 compliant for

TABLE 14.47 Typical properties of generic PSU and PPSU polymers.

	PSU	**PPSU**
Density (g/cm^3)	1.23–1.36	1.29
Melt flow rate (MFR) (g/10 min)	3–90	7–37
Water absorption: 23°C, 50% RH (%)	0.1–0.6	0.35–0.6
Water absorption: 24 h, immersed (%)	0.29–0.3	0.28–0.39
Tensile strength: Yield (MPa)	47.9–75.2	55.2–80
Tensile strength: Break (MPa)	55.2–75.2	69.6–77.9
Tensile elongation: Yield (%)	4.8–6	7–90
Tensile elongation: Break (%)	6.3–13	38–90
Tensile modulus (GPa)	1.8–2.6	2.27–2.28
Flexural strength (MPa)	71–104.8	88.3–111
Flexural modulus (GPa)	2–2.48	2.4–2.76
Charpy notched impact strength (kJ/m^2)	3.4–8	10–64.9
Notched izod impact (kJ/m^2)	5–6.3	2.9–27.3
Rockwell hardness	119–121	119–120
Coefficient of friction	0.09–0.23	
Deflection temperature under load: 0.45 MPa (°C)	177–185.5	141–175
Vicat softening temperature (°C)		207–223
Melting temperature (°C)		218–220
Thermal conductivity (W/mK)	0.245–0.317	0.04–0.35
Surface resistivity (Ohm)	10^4–$3 \cdot 10^{16}$	10^3–10^{16}
Dielectric constant	2.8–3.11	1–3.9
Transmittance (%)	45–90.7	50–90
Haze (%)	0.5–15	

Adapted from Refs. [503–506].

medical applications and meet the FDA and European regulations concerning plastic materials and articles coming into contact with food [507].

The main limitations of PSU and PPSU are low resistance to polar organic solvents, such as esters and ketones, chlorinated hydrocarbons. They also have low UV-light stability and can become brittle quite rapidly if they are exposed to atmospheric conditions.

14.4.3.4 Processing

The melt rheology behavior of PSU is characterized by relatively weak response to shear, and is very similar to flow behavior of PC [495]. PSU can be molded into high-quality engineering parts and high-load mass-produced articles. It can be processed by almost all the techniques adopted for thermoplastics. The most important technique is injection molding. PSU molded parts have excellent dimensional stability and remain strong, rigid, and tough up to temperatures close to the Tg [508].

Before processing PSU must be dried to remove moisture, though water does not react with the PSU, it can cause foaming of the melt during melt processing. This is then evident as surface defects (bubbles, streaking, splay marks) [495]. Higher melt temperatures should be avoided due to the risk of thermal degradation of the polymer [499].

Extrusion, also called extrusion molding, describes a continuous process for manufacturing profiles, monofilaments, plates, or foils from thermoplastic polymers. Thereby, the plastic granulate is melted in barrels containing a screw, pressed through a hot, molding die, and then cooled down. They can be extruded into sheets, film, tubing, rods, slabs, wire, and monofilaments [509].

Processing conditions for PPSU extrusion according to Ref. [508] are:

- predrying: 4 h at 171°C,
- melt temperature: 280−340°C,
- screw design (L/D ratio) of 26:1.

Most of the finishing operations for thermoplastics can be applied, such as annealing, metalizing, machining, joining, etc. PSU can be annealed at temperatures of 160−170°C, PPSU at 190−200°C to enhance environmental resistance, increase stiffness, reduce creep, and enhance resistance to dimensional changes at elevated temperatures [495].

14.4.3.5 Applications

Both, PPSU and PSU are amorphous, heat-resistant, high-performance polymers with high thermal, oxidative, and hydrolytic stability. Their excellent performance characteristics have led to different applications in the automotive and transportation sectors. PPSU is used for components that are exposed to high temperatures and corrosive media because it has exceptional chemical resistance. Examples include pipe fittings, battery containers, medical device parts, and sterilizable products for health care [502]. It is used in the automotive and aerospace industries for applications where superior thermal and mechanical properties relative to conventional resins are required [502]. PSU and PPSU are used for applications in which other plastics, e.g., PA, PC, and PET, fail to meet the requirements. They can replace thermosets, metals, and ceramics. They are used in the food and household sectors as a substitute for glass, metal, ceramic, and porcelain [508].

Both, PSU and PPSU have an extremely favorable combination of properties: good insulation properties, high breakdown rating, favorable dielectric values, outstanding mechanical properties even at elevated temperatures, high long-term service temperature, and very good fire behavior that are important for applications in electrical engineering and electronics [508]. Medical applications are also important area of their applications. PSU and PPSU withstand most sterilization options: heat, steam, boiling water, gamma radiation, and many chemical disinfectants [495]. They are sterilization capable, including EtO gas, radiation, steam autoclaving, plasma, dry heat, and cold sterilization [510]. As high-performance polymers, they both successfully entered in the AM market.

14.4.3.6 Recycling

PAESs are 100% recyclable, either mechanically or as feedstock, and energy from waste can be recovered at incineration plants. The most appropriate recovery options depend on legislation, plastics part design, access to sorting facilities, and regional logistics and recycling costs. Unmixed, clean PSU and PPSU scraps from the manufacture of injection moldings or extrusion can be reprocessed. They can be used as regrind and returned for reprocessing. Unmixed moldings can likewise be processed into new parts after they have been milled and cleaned [511].

Recycled material consisting of sprues, rejects, and the like can be recycled in limited amounts (up to about 20%), provided it has not been contaminated and the material was not thermally degraded during previous processing. The addition of recycled to virgin granules can alter the feed, flow, and demolding characteristics, as well as the mechanical properties, and in particular the impact strength. Therefore, for high-quality engineering components only virgin material should be used [508].

14.4.3.7 3D printing

The key features of PSU and PPSU, such as temperature independent properties, very high long-term service temperatures, good dimensional stability, high stiffness, mechanical strength, and excellent hydrolysis resistance make them suitable candidate for FDM printing [508]. The material has an excellent adhesion between layers which results in great improvement of the impact resistance, strength, durability, and the printing process. Compared to other materials PPSU is rather difficult to print. Recommended print settings are shown in Table 14.48.

PSU and PPSU absorb moisture. It is important to predry the material before processing (150°C for 3 h) and to have control over entire build chamber temperature, nozzle, and build plate. A proper crystallization in 3D printed parts must be obtained [507]. Due to the rigid breakaway support structures, PPSU is not suitable for complex assemblies [514]. Tips for printing, as well as advantages and disadvantages of PSU and PPSU, are presented in Table 14.49.

Typical properties of 3D printing PSU and PPSU filaments are given in Table 14.50. Because of excellent thermal and chemical resistance PSUs are well suited for demanding applications in automotive, aerospace, electronics, defense, foodservice, industrial, plumbing, medical, and semicon applications [510]. Excellent dimensional stability is important for highly reproducible part-to-part dimensions. PPSU considered as one of the highest performance

TABLE 14.48 Print settings for PSU and PPSU.

	PSU	PPSU
Print temperature (°C)	350–380	360–390
Bed temperature (°C)	140–160	140–160
Print speed (mm/s)	20	20
Bed adhesion	PEI sheet, PVP glue stick, PI tape, lightly sanded FR4, or perfboard	PEI sheet or tape (such as Ultem), PI tape, lightly sanded FR4, or perfboard
Cooling fan	No	No
Enclosure	Recommended	Recommended

Adapted from Refs. [510,512,513].

TABLE 14.49 Advantages and disadvantages of PSU and PPSU.

	PSU
PROS	• High strength and stiffness, even at elevated temperatures • Excellent hydrolytic resistance • High continuous use temperature • High resistance to gamma radiation and is sterilization capable • Excellent dimensional stability • Transparent • More affordable than PEEK or PEI • Very little warping
CONS	• Lack of solvent resistance • Poor weatherability • Subject to stress • High processing temperature
TIPS	• PSU requires significantly higher temperatures and higher rotational force in order to be processed successfully. • Poor surface finish can be avoided with the increase of head temperature, reduce extrusion rate. • Porosity can be avoided by decrease of head temperature to prevent decomposition of material or by the change of in-fill pattern. • Warpage, because of nonuniform cooling, can be avoided by increase of build plate temperature and/or ambient temperature.
	PPSU
PROS	• One of the strongest 3D printing thermoplastics for engineering applications • High chemical and heat resistance • Strong and durable • Very high notched impact strength • High environmental stress crack resistance • High heat deflection temperature • Design flexibility
CONS	• High costs • High level of expertise required to achieve successful printing results • A limited number of FDM 3D printers on the market • Thick sections can result in voids • Low resistance to organic solvents and hydrocarbons
TIPS	• Printability is high and it is a comparatively easy material to work with, but requires equipment with high temperature capabilities. • Excellent temperature control for the printing head is also important as it prevents overheating and excessive residence time when the printhead is stationary. • Drying prevents defects such as bubbles or voids, splay, and overall surface roughness, that affect mechanical properties. • The tool path and the speed must be optimized so that the layers cool at an appropriate speed to allow adhesion between them. Long distances and slow print speeds may result in too much cooling and a lack of adhesion between layers. • However, if cooling is too slow, adequate solidification may not take place which will result in a deformed or collapsed part. • With annealing in a hot-air oven any printed-in stresses can be reduced.

Adapted from Refs. [430,510,515–519].

TABLE 14.50 Properties of 3D printing PSU and PPSU filaments.

	PSU	PPSU
Density (g/cm^3)	1.24	1.29
Melt flow index (g/10 min)		14–20
Water absorption: 23°C, 50% RH (%)		0.37
Tensile strength: Yield (MPa)	75	74
Tensile strength: Break (MPa)	52	69.6
Tensile elongation: Yield (%)	6	7.2
Tensile elongation: Break (%)	8	60–120
Tensile modulus (GPa)	2.1	2.34
Flexural strength (MPa)	87	91
Flexural modulus (GPa)	2.05	2.41
Charpy notched impact strength (kJ/m^2)	5.5	75
Deflection temperature under load: 0.45 MPa (°C)	172	207
Surface resistivity (Ohm)	$>10^{13}$	
Volume resistivity (Ohm•cm)		$9 \cdot 10^{15}$
Dielectric constant	3.04	3.44

Adapted from Refs. [513,521–523].

polymers is designed specifically for 3D printing the highest performance parts possible. It is used for manufacturing end use parts especially for general industry and specifically for automotive parts, racing, and research for automotive [507]. In 3D printing PPSU is suitable for manufacturing of concept modeling, functional prototyping, manufacturing tooling aids, and production parts [520].

14.5 Polymer composites

Today, several methods of printing polymer composites using 3D technology are available, one of them is FDM. Manufacturing a composite structure with a single nozzle uses a filament, which besides polymeric material contains an additive: rubber microspheres, particles of glass or metals, fibers, wood flour, etc. The biggest limitation to this method is the availability of such material, as currently the market offers a limited quantity of composite filaments [524].

The FDM process can be utilized to print reinforced plastics by adding fibers into the thermoplastic filament. For FDM processing polymer pellets and fibers are mixed in a blender first and then delivered to extruder to be fabricated into filaments. Typical short fibers used as reinforcement to improve mechanical properties of 3D printable filaments are glass and carbon fibers [525]. Besides increasing mechanical properties, the reinforcement may also add extra functionality to the material such as electroconductivity or biocompatibility. The addition of short fibers to the printing filament increases the stiffness of the printed part but the strength increase is still limited as fiber pull out may occur before breakage, and because of the creation of voids in printed object [526]. Besides short fibers, the reinforcement of polymer composites can be achieved by adding continuous fibers, such as Kevlar or GFs.

Due to their low cost, particle reinforcements are widely used to improve the properties of polymer matrix. The key issues for particle reinforced composites in FDM include improved tensile/storage modulus by adding iron or copper particles, improved wear resistance by adding aluminum or aluminum oxide, and improved dielectric permittivity by adding ceramic or tungsten particles [525]. The size, shape, and distribution of particles affect the characteristics of polymer composites. By the addition of carbon-based nanomaterials enhanced electrical properties can be obtained and by adding functional inks color changing 3D printable filaments are obtained. In the recent years, a lot of research in the development of 3D printable polymer composites has been undertaken, presented among others by Sing et al. [527] and Penumakala et al. [528]. Several of them, present on the market, are presented in this chapter.

14.5.1 Metal filaments

Metal 3D printing has become increasingly popular, since parts can be serially 3D printed for mass production. 3D-printed products can be up to 60% lighter than their machined counterparts; 3D printing uses less energy and reduces waste to a minimum. Other reason is that each material offers a unique combination of practical and aesthetic properties to suit a variety of products, as prototypes, miniatures, jewelry, functional parts, or even kitchenware [529].

Metal filament is basically polymeric filament with some amount of metal added. They are named "metal fill" or "composite" metal filaments. A variety of companies provide metal filaments with different types and amounts of metal particles embedded into PLA, ABS, or PA polymer matrix. 3D printing metal materials are aluminum, steel, brass, copper, bronze, sterling silver, gold, platinum, and titanium, though the mostly used in composite filaments are copper, bronze, iron, and stainless steel [529,530].

As metal is more dense than polymer, it adds weight to the filament. Metal filaments are brittle and need additional care and handling when printing as well as with the printed objects. Printed objects feel more solid, and the look is very similar to cast metal. They can be polished or even caused to "rust," in the case of iron-filled filament. Postprocessing is possible to give a variety of effects. Printed objects can be brushed, polished, sanded, waxed, or coated [530].

However, compared to standard filaments, metal filament can cost up to two to four times more depending on the amount and type of fill [530]. The key advantages of metal 3D printing filament are their unique metallic finish and appearance, high durability, low flexibility, depending on the structural design and low solubility. They are ideal for jewelry, statues, home hardware, or replica artifacts [530].

Stratasys has developed an aluminum-filled PA 12 material that offers mechanical advantages and a metallic appearance. By fusing aluminum into a thermoplastic material, users can obtain parts that are stronger, stiffer, and highly resistant to wear and tear [529].

In metal 3D printing filament, a different amount of metal powder can be present, from 20% to 80%, typically more than 50% [530]. Companies ColorFabb, ProtoPasta, Amolen, FormFutura, Gizmo Dorks, and TreeD filaments offer composite metal—PLA filaments. These are filaments that contain a significant percentage of metal powders to have the look, feel, and weight of a metallic object and still can be printed at low temperature (200—300°C). The iron-based filaments even form rust in certain conditions. They are polished to expose metal, which is then treated with water or vinegar to cause different aging effects [530]. Lower percentage of fill content (20%) of copper or bronze keeps the cost down and still provides a nice metallic look. This option may be easier to work with than some of the other more brittle metals containing more metal fill. Bronze-filled filament by its color looks almost like gold. With a higher percentage of metal fill, i.e., 80%, the filament is heavier and more brittle [530]. Metal 3D printing filaments from ProtoPasta are manufactured by adding 70%—80% of metal powder by weight, which is approximately 30%—40% by volume to the PLA. Treating printed objects with heat (110°C for 10 min) makes them significantly stronger and harder [531].

Metal filaments are not easy to print. Because of metal powder fill printing difficulty is high, requiring fine-tuning of nozzle temperature, flow rate, and postprocessing. The more metal powder present in the filament, the more difficult it may be to find the correct settings to get a good print [529].

Recommendations for printing settings according to Ref. [530] are:

- print temperature: 190—220°C; 215—235°C (copper, bronze),
- bed temperature: not needed; 0—60°C,
- print speed: 30 mm/s; 40—100 mm/s,
- bed adhesion: PI or PEI tape, blue painter's tape, glue stick,
- cooling fan: 50%—100%,
- enclosure: not required.

Considerations must be made for adjusting temperature, retraction, and first-layer thickness. Heated bed is not required and there is minimal shrinkage during cooling. Also warping is minimal [529]. In metal filaments the heat travels through filament more efficiently because of the metal particles present. Because of this it will heat up easier in hotend and it will cool down faster when leaving the nozzle. The better cool down properties means good performance on overhanging parts [529]. Another issue is need for upgrade 3D printer nozzle to stainless steel or other hardened alloys. Brass print nozzles wear out much faster due to the abrasive metal fill [529].

TABLE 14.51 Advantages and disadvantages of metal filaments.

	Metal filaments
PROS	• Extremely durable • Not soluble • Unique metallic appearance and finish • Little to no shrinkage while cooling • No heated print bed needed • Does not need high-temperature extruder • Heavier than standard filaments
CONS	• Not easy to print with • Need to fine-tune nozzle temperatures • Need to regulate flow rate • Requires a wear-resistant nozzle • Printed parts are very brittle • Very poor bridging and overhangs • Can cause partial clogs over time • Expensive
TIPS	• Because filament heats up easier in the nozzle it can be printed at lower temperatures and at relatively high speeds. • Needs a bit more flow compared to normal PLA settings. • Parts with lots of large bridging regions will be very difficult to print – need for adjusting a speed and extrusion rate and to find specific fill angle that will work best. • As is easy to sand down, carefulness not to lose too much details is recommended. • Retraction of filament is rather challenging. To avoid blobs at the beginning and end of each printed segment, reducing the pressure in the nozzle right before the end of a print segment and setting "extra restart distance" to a negative value of −0.1 or −0.2 mm is recommended.

Adapted from Refs. [532–534].

TABLE 14.52 Properties of 3D printing metal filaments.

	Bronze 80 w%	**Copper 80 w%**	**Steel 80 w%**
Density (g/cm^3)	3.9; 3.5	4; 3.4	3.13
Water absorption: 23°C, 50% RH (%)	0.3	0.3	0.3
Tensile strength: Break (MPa)	30; 19	25; 18.3	23
Tensile elongation: Break (%)	5–10	3–10	1–3
Tensile modulus (GPa)	3.99	4.21	
Flexural strength (MPa)	40	40	30
Flexural modulus (GPa)	9	7	3
Notched izod impact (kJ/m^2)	10; 11.3	10; 9.3	10
Vicat softening temperature (°C)	65		
Melting temperature (°C)	150–170	150–170	150–170
Thermal decomposition (°C)	>240	>240	>240

Adapted from Refs. [535–539].

Printing tips, advantages, and disadvantages of metal filaments are given in Table 14.51. In Table 14.52 typical properties of metal filaments, filled with bronze, copper, or steel particles are presented. In Fig. 14.24 Proto-Pasta's steel-filled composite PLA filament before and after postprocessing is shown.

14.5.2 Magnetic filaments

Magnetic filaments are niche products, belonging to specialty filaments. They are usually manufactured with iron, graphene, or other metal additives which makes the material magnetic. Depending on the concentration of

FIGURE 14.24 3D-printed object from steel-filled PLA printing filament. *Image credits: ProtoPlant, makers of Proto-Pasta.*

metal in a composite, it also may share other properties of metal like color, and the ability to be polished or rusted [540].

One of the first publications detailing with 3D printing magnets is from the Vienna University of Technology. They printed magnets using custom magnetic filament and a commercially available FDM printer [541]. At MIT, researchers have combined a magnetic 3D printing ink and magnetic field applied during extrusion to control the magnetic directions of 3D printed regions of soft magnetic materials [542].

Usually, magnetic filaments are made by mixing finely ground iron powder with the polymeric material, such as PLA or ABS. The magnetic filament products available in the market today are based mainly on PLA. Despite the name, this 3D printing filament type is actually *ferromagnetic*, meaning that has magnetic properties, and is attracted to magnetic fields, but has no fields of its own [60]. Induction at magnetic saturation is about 0.15 T [543]. Magnetic 3D printing filament based on PLA or ABS, infused with powdered iron, features a grainy, gunmetal finish, and it sticks to magnets [60]. Magnetic filaments can be used to make various mechanical and engineering parts. Replacement parts of magnetic sensors and actuators for automated systems can be easily printed, instead of having to order new parts. Magnetic prints have made their way to home fixtures, toys, fashion accessories, and costumes [544,545].

The prints have good rigidity and can handle minor overhang features with no problems. Prints made from magnetic filaments can have either matte or glossy finishes depending on the printing temperature. Either way, magnetic prints end up with a striking and unique finish. A finishing method that can only be uniquely done with magnetic filament prints is rusting [544].

The recommended printer settings are similar to those of the base material, PLA. A printing temperature within the range of 215–225°C should be further set depending on the ratio of PLA to iron in the filament. A heated bed is not necessary when printing with magnetic filaments, but mostly temperature of around 60°C is used. Rapid cooling tends to result in warping when printing with magnetic filaments [544].

Recommendations for printing settings according to Refs. [544,545] are:

- print temperature: 215–225°C,
- bed temperature: not needed; 0–60°C; 60°C is optimal,
- print speed: 60–80 mm/s,
- bed adhesion: blue painter’s tape,
- cooling fan: not recommended; a setting of 10%–20%,
- enclosure: not required.

Magnetic filament is quite rigid because of the powdered iron infused with the polymer matrix. This also makes it too brittle to negotiate very tight corners along the filament path of some printers. As with other infused filaments, the powdered iron in magnetic filaments is hard and can be very abrasive.

Prints made from magnetic filaments are probably a little weaker than those made from standard PLA. Magnetic filaments also cannot act as suitable replacements for truly conductive materials since the iron powders are too small and isolated from each other in a matrix made from nonconductive PLA [544].

TABLE 14.53 Advantages and disadvantages of magnetic filaments.

	Magnetic filaments
PROS	• Very strong and extremely durable • Good rigidity • Not soluble • Little to no shrinkage
CONS	• Inflexible • Fine-tuning of nozzle temperature, flow rate, and postprocessing • Quite abrasive • Expensive • Not food safe
TIPS	• To avoid warping cooling fan is not recommended, at least for the first two layers; setting to 10%–20% may be used afterward. • Print speed of 10–20 mm/s is recommended for the first two layers. • To avoid under-extrusion or clogging printer temperature must be 20–40°C higher than the print temperature for PLA. • A wide nozzle is recommended, about 0.4 mm. • To avoid filament break during printing, the filament path should consist of smooth and gentle curves from spool to the nozzle.

Adapted from Refs. [532,544].

TABLE 14.54 Properties of 3D printing magnetic filament.

	Iron/PLA
Density (g/cm^3)	1.8
Tensile strength: Break (MPa)	48
Tensile elongation: Break (%)	31
Flexural strength (MPa)	80
Deflection temperature under load: 0.45 MPa (°C)	65

Adapted from Ref. [546].

Printing tips, advantages, and disadvantages of magnetic filaments are given in Table 14.53. In Table 14.54 typical properties of magnetic filaments are presented.

14.5.3 Conductive filaments

Electrically conductive materials in 3D-printed applications are based on metal-ion or metal-colloid inks or are carbon-based conductive composites. Conductive filaments are not very common yet, and practically all that are available in the market are composed of a mixture of carbon in the form of graphene and polymeric material, mostly PLA or ABS, but also TPU and HIPS [547]. Carbon-based polymer composites are advantageous over metal-based or metal-alloy colloid inks [548]. Carbon-based polymer composites typically do not need additional processing step after printing such as thermal annealing or evaporation of solvent as required by 3D printing of metal-ion and metal-colloid inks, and they have significantly longer shelf life than that of metallic ink [548,549].

Conductive filaments enable many exciting new design opportunities for 3D printing. They can be used to create touch sensors in applications that require human interface devices like gaming pads and MIDI machines or conductive traces in wearable electronic devices and creating interfaces between computers, Arduino boards, and other components to build elaborate DIY projects [550]. The field of wearable electronics is often cited as one of the best potential beneficiaries of the technology of conductive 3D printing. By using conductive filaments, electrical circuits can be seamlessly blended into practically any clothing fabric [547]. The prints made from conductive filaments can also be effectively used as electromagnetic and radiofrequency shields applied in the telecommunications field, and in the maintenance of sensitive measuring equipment such as those found in industrial and scientific laboratories [547]. A resistivity of 15 Ω cm allows it for lighting up LEDs, operating capacitive sensors, and for powering low voltage circuits. Conductive PLA filament is more flexible than pure PLA, but has less layer adhesion. Printed parts are rigid if more than a mm or 2 thick. Thin sections are somewhat flexible but fail along layer lines if flexed more

TABLE 14.55 Advantages and disadvantages of conductive filaments.

	Conductive filaments
PROS	• Very low warping • Not soluble • Allows low-voltage electronic circuits • Does not require a heated bed
CONS	• Not durable and not so flexible • Repeated bending may break the material • Shrinks during cooling • Not safe with food • Expensive
TIPS	• Special handling to ensure that the filament does not break, which includes providing a smooth path from the spool to the extruder. • A temperature up to 50°C is sufficient if a heated bed is used. • In addition to using an abrasion-resistant nozzle, using a wide nozzle, greater than 4 mm, is recommended.

Adapted from Ref. [532].

than a few times [551]. Similar to other fused material filaments, conductive filaments are usually more brittle than their standard plastic counterparts.

The printing temperature for each conductive filament depends on the base polymer. For instance, the PLA-based conductive filament has a recommended printing temperature of 220–230°C, the ABS-based conductive filament up to 260°C. A heated bed is usually not necessary for PLA-based filaments, but may help in reducing warping of the final print. Any method of bed adhesion that works for the base resin should be effective for the conductive filament too [547]. Some tips for printing are given in Table 14.55.

Recommendations for printing settings according to Ref. [60] are:

- print temperature: 225–260°C (PLA-based),
- bed temperature: 50–60°C; 90–110°C,
- print speed: 20–80 mm/s; 30–70 mm/s,
- bed adhesion: PI tape, hairspray,
- enclosure: required.

The essential limitation of conductive filaments is that they are not as conductive as metals. They are also quite expensive, especially compared to standard ABS or PLA filaments. Conductive ABS is stronger and more heat resistant than the PLA variant, but it comes with the same fume problems as normal ABS [550]. Advantages and disadvantages of conductive filaments are given in Table 14.55, and some typical properties of conductive filaments are presented in Table 14.56. In Fig. 14.25 electrically conductive composite PLA filament is shown.

TABLE 14.56 Properties of 3D printing conductive filament.

	Iron/PLA
Density (g/cm^3)	1.34
Melt flow index (g/10 min)	12.5–18.5
Tensile strength: Break (MPa)	15.3
Tensile elongation: Break (%)	5.4
Flexural strength (MPa)	24.6
Flexural modulus (GPa)	1.02
Notched izod impact (kJ/m^2)	3.7
Deflection temperature under load: 0.45 MPa (°C)	65
Melting temperature (°C)	170–240

Adapted from Ref. [552].

FIGURE 14.25 3D-printed objects made from conductive composite PLA printing filament. *Image credits: ProtoPlant, makers of Proto-Pasta.*

14.5.4 Carbon fiber filaments

CF filaments refer to a class of filaments made from different base materials that have tiny CFs infused in them in order to improve the properties of base materials [553]. Several popular filaments can be produced with CF fill including PLA, PETG, PA, ABS, PC, as well as high-performance polymers, such as PEEK, PEKK, or PEI [554].

CFs are composed of carbon atoms bonded together in a crystalline formation. The crystal alignment gives the fiber an excellent strength-to-volume ratio. CF adhered together using a bonding agent, the fibers distribute load smoothly and form an incredibly strong, light composite material. These CF composites come in the form of sheets, tubes, or custom molded features and are used in industries like aerospace and automotive in which strength-to-weight ratio is important characteristics [555].

In 3D printing, chopped CF-filled polymer base material and continuous CF-reinforced polymer are used. Chopped CF-filled thermoplastics are printed using a standard FDM (FFF) printer. They are comprised of a thermoplastic (PLA, ABS, or PA) reinforced with tiny chopped strands of CF, giving typically weaker materials added strength. The chopped fibers increase the strength and stiffness of the printed object, as well as improving its dimensional stability, surface finish, and precision [555]. The 3D-printed parts are much lighter and more dimensionally stable, as the fibers help prevent shrinking of the part as it cools [554]. It is important not to add too much fibers into the polymer matrix, because these can detrimentally affect the overall quality of the piece, decreasing surface quality and part accuracy. Prototypes and end-use parts can be made, as it gives the strength and appearance needed for in-house testing or customer-facing parts [555].

Continuous CF-reinforced filament is a distinct printing process that has continuous strands of fibers laid in a standard thermoplastic base material. It is a cost-effective solution for replacing traditional metal parts with 3D-printed composite parts because they can achieve similar strength at a fraction of the weight. Continuous CF strands are inlaid in thermoplastics using Continuous Filament Fabrication (CFF) technology. Continuous strands of high strength fibers are via a second print nozzle laid within FDM extruded thermoplastics while printing. The reinforcing fibers form the “backbone” of the printed part, yield stiff, strong, and durable parts [555].

Continuous CF not only adds strength, but it also allows the user to selectively reinforce in areas that require more durability. Within each layer, there are two reinforcement methods: concentric and isotropic. Concentric infill reinforces the outer boundaries of each layer (both internal and external) and extends into the part by a user-defined number of loops. Isotropic infill creates unidirectional composite reinforcement on each layer, and can mimic CF weaves by altering the reinforcement direction on layers. These reinforcement strategies enable industries such as aerospace, automotive, and manufacturing to integrate composites into their workflow in a new way. Printed parts excel as tools and fixtures such as end-of-arm tooling, soft jaws, and CMM fixtures [555].

High-modulus CF incorporated into engineering and high-performance resins are ideal for applications that require exceptional stiffness, ease of printing, improved dimensional stability, UV resistance, and lighter weight parts versus standard structural materials [556]. These CF filaments have unique strength and rigidity, but their carbon component is too small to afford conductivity.

Print settings, such as printing temperature, speed, bed adhesion, and extrusion rates, are very similar to the normal settings used for the base polymeric material that the fibers were added to. However, due to the added fibers, these specialty materials are more likely to clog and can require special hardware to avoid damaging the printer [554].

CF PLA filament shares similar properties with standard PLA filament but it is stiffer. It is also rigid and has superior layer adhesion. It is used for producing high-quality and strong objects, like protective casings, various mechanical parts, and many other high durability uses. It also offers more dimensional stability, which means warp-free printing. The downside of CF filament is that its abrasive nature speeds up the wear and tear of printer nozzles, especially those made of brass [532].

Recommended 3D printing conditions for PLA-based CF filaments according to Refs. [532,554] are:

- print temperature: 200–230°C,
- bed temperature: optional; 45–60°C; 60°C is optimal,
- print speed: 60–80 mm/s,
- bed adhesion: blue painter’s tape, PEI, glue stick,
- cooling fan: required,
- enclosure: not required.

Advantages and disadvantages of PLA-based CF filaments and tips for printing are presented in Table 14.57.

CF filaments have different advantages depending on base polymer. If the strength is the main criteria, then CF PA would be the material of choice. However, if stiffness is the main driver, then CF PETG is the best solution. However, if short-term thermal properties are main concern, then CF ABS is the best choice.

CF-reinforced ABS filament is ideal for manufacturing a structural component with high modulus, excellent surface quality, dimensional stability, lightweight, and ease of printing [558]. CarbonX CFR-ABS is made using 15% high-modulus CF. Compared to ABS it has 85% improvement over unfilled ABS in flexural modulus and 77% in tensile modulus [558].

Recommended 3D printing conditions for ABS-based CF filaments according to Ref. [559] are:

- print temperature: 220–240°C,
- bed temperature: 100–110°C,
- print speed: 50–70 mm/s,
- bed adhesion: PI tape, ABS/acetone slurry.

TABLE 14.57 Advantages and disadvantages of PLA-based CF filaments.

	CF PLA
PROS	• Increased strength and stiffness • Used for quality parts • Very good dimensional stability • No heated bed needed • Little warping and shrinkage during the cooling process
CONS	• Material contains abrasive strands • Increased oozing while printing • Increased brittleness of filament • Higher tendency to clog • Excessive wear on printer nozzles, especially brass • Regular users need to invest in harder metals for print nozzles
TIPS	• Ideal layer height is 60% of nozzle diameter. • Hardened nozzle with 0.4 mm orifice or larger is recommended. • Printing layers below 0.25 mm may create too much back pressure in the hotend and result in poor feeding, jams, drive gear clicking, and eating a notch into the filament. • Retraction of filament must be reduced to avoid the change of a buildup of fibers inside the extruder assembly. • Slower print speed helps by pushing small clogs through the nozzle if they start to form.

Adapted from Refs. [532,554,557].

PETG reinforced with high-modulus CB has superior chemical resistance versus ABS, and three times lower moisture absorption than ABS. It has low and near isotropic shrinkage and very low odor emitted during printing [560].

Recommended 3D printing conditions for PETG-based CF filaments according to Ref. [560] are:

- print temperature: 230–260°C,
- bed temperature: 70–90°C,
- print speed: 50–70 mm/s,
- bed adhesion: clean glass/PI tape, PVA-based glue, hairspray.

PC-based filaments offer some of the highest thermal performance on the 3D market. A high-performance CF-reinforced PC filament is known for its high heat performance, high stiffness, excellent surface quality, and dimensional stability [561].

Recommended 3D printing conditions for PC-based CF filaments according to Ref. [561] are:

- print temperature: 280–310°C,
- bed temperature: 110–120°C,
- bed adhesion: PEI sheet or tape, PI Tape, glue stick on clean glass, ABS/acetone slurry.

PA 6 reinforced with high-modulus CF is used to produce a component with high modulus, improved chemical and thermal resistance, excellent surface quality, and ease of printing. At CarbonX CF-Nylon excellent dimensional stability comes from the CF and the semiaromatic PA. Higher HDT (147°C at 0.45 MPa) allows for expanded use in high-temperature applications [562].

Recommended 3D printing conditions for PA-based CF filaments according to Ref. [562] are:

- print temperature: 240–270°C,
- bed temperature: 80–100°C,
- bed adhesion: PI tape, clean glass with ABS/acetone slurry.

CF-reinforced PEEK is one of the premier polymers in FDM 3D printing, made using high-modulus CF for exceptional stiffness, strength, and dimensional stability. PEEK is used in some of the most demanding applications such as seals, gears, bushings, bearings, and pump and compressor components. CF-reinforced PEEK filament with near zero moisture absorption shows high thermal and excellent chemical resistance, as well as superior wear resistance [563].

PEEK has a melt temperature (T_m) of 343°C; therefore, an all-metal extruder capable of reaching (and holding) temperatures upward of 400°C is needed [563].

Recommended 3D printing conditions for PEEK-based CF filaments according to Ref. [563] are:

- print temperature: 380–410°C,
- bed temperature: 130–150°C,
- bed adhesion: PEI sheet or tape.

With CF-reinforced PEKK filament has outstanding mechanical, thermal, and chemical resistance, as well as excellent resistance to a broad range of chemicals, such as those used in the oil/gas, automotive, aerospace, industrial, and chemical processing industries. CF-PEKK filament has a wider processing window than PEEK and typically prints with extruder temperatures between 360 and 390°C, whereas CF-PEEK often requires extruder temperature above 400°C. It also has a lower rate and degree of crystallinity than CF-PEEK filament, which helps at ease of printing. However, once printed and annealed, PEKK parts exhibit superior performance versus PEEK [564].

Recommended 3D printing conditions for PEKK-based CF filaments according to Ref. [564] are:

- print temperature: 355–385°C,
- bed temperature: 120–140°C,
- bed adhesion: PEI sheet or tape,
- enclosure: required.

PEI filaments have excellent mechanical, thermal, and chemical resistance properties and offer the ability to create parts with excellent properties at elevated temperatures. The addition of high-modulus CF greatly increases the stiffness/modulus of the material and improves dimensional stability during and after printing [565]. PEI-based CF filaments provide for automotive/transportation applications a high performance, chemically resistant, thermally stable, cost-effective alternative to metal that is strong enough to replace steel in some applications and light enough to replace aluminum in others. It is also an excellent material for today's demanding electrical applications,

TABLE 14.58 Properties of 3D printing CF-reinforced PLA, ABS, PC, and PETG filaments.

	CF-PLA	CF-ABS	CF-PC	CF-PETG
Density (g/cm^3)	1.29	1.11	1.36	1.34
Tensile strength: Break (MPa)	48	44	70	55.5
Tensile elongation: Break (%)	2	1.8	2	2.5
Tensile modulus (GPa)	4.95	4.02	6.2	4.93
Flexural strength (MPa)	89	76	90	80
Flexural modulus (GPa)	6.32	5.26	5.89	5.74
Heat deflection temperature: 0.45 MPa (°C)	91	102.5	135	77
Glass transition temperature (°C)	60	105	143	80
Surface resistivity (Ohm/sq)	$>10^{9}$	$>10^{10}$	$>10^{9}$	$>10^{10}$

Adapted from Refs. [566–569].

TABLE 14.59 Properties of 3D printing CF-reinforced PA, PEEK, PEKK, and PEI filaments.

	CF-PA	CF-PEEK	CF-PEKK	CF-PEI
Density (g/cm^3)	1.17	1.39	1.38	1.31
Tensile strength: Break (MPa)	63	105	115	145
Tensile elongation: Break (%)	3	3	3	1.5
Tensile modulus (GPa)	3.8	8.1	9.56	7.7
Flexural strength (MPa)	84	136	135	120
Flexural modulus (GPa)	3.75	8.3	9.85	7.5
Heat deflection temperature: 0.45 MPa (°C)	147	265	280	205
Glass transition temperature (°C)	70	143	165	217
Surface resistivity (Ohm/sq)	$>10^{9}$	$>10^{9}$	$>10^{9}$	$>10^{9}$

Adapted from Refs. [570–573].

including connectors, MCB components like housings, shafts, and levers, hard disk drive internals, and many other applications [565].

Recommended 3D printing conditions for PEI-based CF filaments according to Ref. [565] are:

- print temperature: 360–390°C,
- bed temperature: 140–160°C,
- bed adhesion: PEI tape, PI tape, lightly sanded glass-reinforced epoxy laminate (FR4), or perfboard.

Some typical properties of CF-reinforced filaments are given in Tables 14.58 and 14.59. In Fig. 14.26 3D printing CF-reinforced PA filament is shown.

14.5.5 Glass fiber filaments

GF-reinforced plastic materials have received increasing attention mainly due to their superior mechanical performances which make them as good substitutes for engineering plastics or metals [574]. GF-reinforced polymer composites have been prepared by various manufacturing technology and are widely used for various applications. GFs have excellent properties like high strength, flexibility, stiffness, and resistance to chemicals

FIGURE 14.26 3D-printed object from CF-reinforced PA filament. *Image credits: Fusion3.*

[575]. The mechanical strengths of long GF-reinforced materials are superior to those of short GF-filled materials. As an example, PP resins reinforced with 60–70 wt% of 6–8 mm long GF have been widely used in the automotive industry [574].

In 2015, company 3Dom USA released Glass Filled PLA filament, which is a composite of regular PLA and GF, and has superior properties to neat PLA, while also being quite low in price. This material is stronger, tougher, and more flexible than neat PLA. With 57 MPa tensile strength is 40% stronger than PLA, 30% tougher, and has 34 J/m of impact strength. Additionally, the material is quite flexible (two times that of PLA) and can achieve a tensile elongation of 3.4% prior to failure. Similar to PLA, Glass Filled PLA possesses the sought after attributes of low warp occurrences, as well as a lack of any noticeable odor. It can be printed at a temperature of around 190–210°C, and without a heated build platform. Printed objects have nice surface finish, which is similar in appearance to ceramics [576].

NylonG is GF infused 3D printing PA 6 filament that has excellent tensile strength and impact resistance, very little flex, and retains dimensional accuracy better than neat PA 6 [577]. It also has excellent interlayer adhesion. The GF specifically adds much more impact resistance to printed parts, making this filament great for creating parts that need to stand up to a beating or need to absorb large amounts of kinetic energy. Under repeated shock, GF-reinforced NylonG 3D prints maintain their shape and structural integrity. 3D-printed parts are durable, stable, and can protect components susceptible to shock and impact better than any other engineering-grade filament [577].

Fiberglass is thin strands of glass bundled together into a fiber, traditionally used in composites for boat, automobile, and aircraft manufacture. It has flexural strength of 210 MPa and a tensile strength of 590 MPa [578]. Fiberglass is reinforcement option for 3D printing filaments that has a bit more flex and energy return to it, than CF. 3D-printed fiberglass is 11 times more rigid than ABS and 26 times more rigid than PA. Fiberglass-reinforced PA 6 is cost effective, and as strong as CF-reinforced filament; this material is 60% less stiff, and two times heavier. It is best used in intermittent loading conditions, and bends until eventual fracture. Fiberglass is great for production of sturdy parts, and it is the most cost-effective reinforcement option [579,580]. Mostly, it is applied for functional prototypes, jigs, fixtures, custom end-use production parts, and structural parts [578].

Recommended 3D printing conditions for PA 6–based GF filament (GF30-PA6) according to Refs. [581–583] are:

- print temperature: 260–280°C; 255 ± 10°C; 280–300°C,
- bed temperature: 60–75°C; 25–50°C,
- print speed: 60 mm/s,
- bed adhesion: hairspray, perfboard, PEI sheet,
- cooling fan: not needed,
- enclosure temperature: not needed, environment temperature (25–50°C).

Both, GF- and CF-reinforced 3D printing filaments are a new step in the direction toward cost-efficient, automated, and larger-scale production. Composites are stiffer and stronger and offer similar formulation, mechanical and chemical properties as injection molding grades.

A heat-stabilized 30% glass-reinforced PA has HDT over 150°C, and is resistant to most solvents, cleaning agents, automotive fluids, and fuels at room temperature [584]. GF-reinforced PP has very high stiffness and strength (up to +250% compared to ABS), large operational temperature range (−20°C to 120°C), and very low moisture absorption [585]. GF-reinforced ABS is very stiff and strong. With such filament different structural parts can be created without lifting and warping that can happen with unfilled ABS.

Recommended 3D printing conditions for ABS-based GF filament (ABS-GF10) according to Ref. [586] are:

- print temperature: 230–245°C,
- bed temperature: 95–110°C,
- bed adhesion: PI tape, PEI tape, or ABS/acetone slurry.

MAX-G GF20 PETG is a structural grade of PETG copolyester reinforced with 20% GF that adds strength and toughness to printed part. GF reduces shrinkage, lifting, and warp. It has superior chemical resistance versus ABS and PLA, three times lower moisture absorption than ABS, and five times lower than PA 6. Printed parts exhibit good resistance to dilute aqueous solutions of mineral acids, alkalis, salts, and soaps, and to aliphatic hydrocarbons, alcohols, and a variety of oils [587]. Filament is suitable for use in practically any desktop 3D printer that has a heated bed.

Recommended 3D printing conditions for PETG-based GF filament (GF20 PETG) according to Ref. [587] are:

- print temperature: 245–260°C,
- bed temperature: 60–70°C,
- bed adhesion: hairspray, perfboard, PEI sheet, PVA glue.

PEEK has exceptional mechanical, thermal, and chemical resistance properties. With the addition of 20% GF a low warp, improved dimensional stability and stronger/stiffer parts are obtained [588]. Material shows excellent resistance to a broad range of chemicals, such as those used in the oil/gas, automotive, aerospace, industrial, and chemical processing industries, making it a go-to material in some of the most demanding applications [588].

Recommended 3D printing conditions for PEEK-based GF filament (GF20 PEEK) according to Ref. [588] are:

- print temperature: 375–410°C,
- bed temperature: 130–145°C,
- print speed: 10–50 mm/s,
- bed adhesion: PEI Tape,
- enclosure temperature: 70–140°C.

PEI is an amorphous, high-performance polymer that combines excellent thermal properties, exceptional dimensional stability, inherent flame retardancy, good chemical resistance, and long-term hydrolytic stability. The addition of 10% of GF adds stiffness, strength, thermal properties, and enhanced dimensional stability. Filament offers the ability to create parts with excellent properties at elevated temperatures due to a high Tg (217°C). Printed parts have highly reproducible part-to-part dimensions [589].

Recommended 3D printing conditions for PEI-based GF filament (GF10 PEI) according to Ref. [589] are:

- print temperature: 370–390°C,
- bed temperature: 120–160°C,
- print speed: 20–30 mm/s,
- bed adhesion: PEI Tape,
- enclosure: warm to hot.

Advantages and disadvantages of GF-reinforced 3D printing filaments, together with printing tips, are given in Table 14.60. Some typical properties of GF-reinforced filaments are given in Table 14.61. In Fig. 14.27 3D-printed object made from GF-reinforced PA filament and 3D-printed object made from GF-reinforced PLA filament are shown.

14.5.6 Ceramic filaments

Ceramic 3D printing filaments extend the range of applications in FDM printing. For ceramic materials to be used in FDM, composite filaments are prepared by densely loading ceramic particles (up to 60 vol%) into thermoplastic materials, for example, ABS filled with 3 μm barium titanate powder up to 35 vol% [594]. Even if the final printed object consists of pure ceramic, the thermoplastic binder system is a temporary vehicle to enable shaping and stabilization of the ceramic particles. The first application of FDM using Al_2O_3 and Si_3N_4 filled binder systems was reported by Danforth in 1995, though the final sintering densities of printed objects were unsatisfactory (75%–90%) [595]. Mechanical properties comparable with other processing routes were achieved for dense structural Si_3N_4 parts

TABLE 14.60 Advantages and disadvantages of GF-reinforced filaments.

	GF filament
PROS	• Improved dimensional stability; glass fibers reduce shrinkage, lift, and warp • Exceptionally stiff and strong, without being brittle • Very strong layer bonding • Ideal for structural engineering–grade applications
CONS	• Very abrasive • Higher wear on printer nozzles • Not suitable for small parts and details
TIPS	• Not recommended for smaller, detailed parts. • A minimum detail size of 0.8 mm is required and a minimum feature size of 3 mm, which allows the fiber to be laid down between the layers of the shell. • Ideal layer height is 60% of nozzle diameter. • For printing with moving and interlocking parts, a 0.5 mm clearance is required for parts to come loose. • Angles greater than 40 degrees usually need supports. • The minimum wall thickness is 3 mm.

Adapted from Refs. [580,581].

TABLE 14.61 Properties of 3D printing GF-reinforced filaments.

	GF-PA 6	PA-fiberglass	GF-PETG	GF-PLA
Density (g/cm^3)	1.2	1.5	1.41	1.32
Tensile strength: Break (MPa)	84.5	590	55	67
Tensile elongation: Break (%)	3.4	3.8	4	1.5
Tensile modulus (GPa)	4.43	21	3.28	5.6
Flexural strength (MPa)	136.4	200	77	
Flexural modulus (GPa)	4.64	22	3.32	
Charpy notched impact strength (kJ/m^2)	16.5			21
Heat deflection temperature: 0.45 MPa (°C)	191	105	70	144
Glass transition temperature (°C)	75		80	60
Melting temperature (°C)	215			175

Adapted from Refs. [590–593].

produced by FDM using filaments of 55–60 vol% ceramic loading [596]. Recently, researcher reported that the filament with a solid content of 50 vol% alumina displayed a good 3D printing behavior and was printable with nozzle sizes down to 150 μm [597].

Current ceramic FDM applications are in the fabrication of bioceramic scaffolds and lattice photonic bandgap structures, and the potential growth lies in the fabrication of functional electronic components [598].

The quality of the printed objects, such as homogeneity, surface roughness, dimensional accuracy, and mechanical properties, also closely depend on the process parameters, including rod width (fused ceramic/polymer filament), layer thickness, building orientation, raster angle, etc. [598]. The main problem is the staircase effect, which is also regarded as the major disadvantage of FDM, as can be easily found in printed ceramic parts. This is predetermined by the size of the extruded filament, resulting in limited control in the z direction [598].

After printing the printed ceramic part is subjected to binder removal and sintering to achieve densification. Structures with sintering densities lower than theoretical density, i.e., 98.4%, are made because during printing process, pores and cavities are introduced [597].

According to Nötzel [597] special properties of ceramic filaments are required to obtain printed ceramics. These are:

- molten feedstock viscosity should be low for low-force nozzle extrusion,
- high strength of feedstock at room temperature for good filament and printed object stability,
- complete debinding and sintering of the parts without deformation,

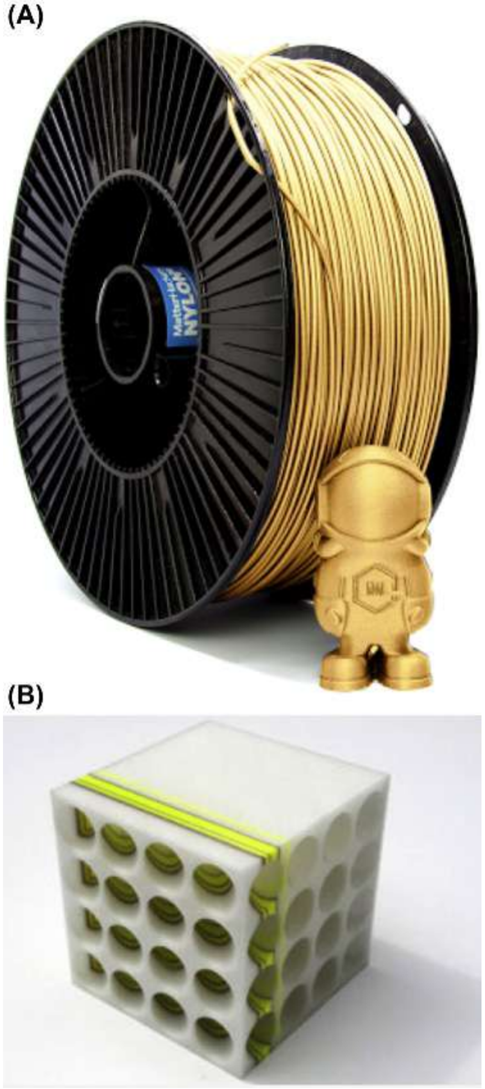


FIGURE 14.27 3D-printed objects from: (A) GF-reinforced PA filament, (B) GF-reinforced PLA filament. *(A) Image credits: MatterHackers Inc. (B) Image credits: Filamania Ltd.*

- solid loads between 45 and 60 vol% for high densities and warpage-free shape after sintering,
- particle sizes of a maximum of 10% of the aspired structural details,
- complete binder wetting of the particles for best deagglomeration.

There are also some hardware requirements: a full metal hotend with short and effective warming zones, pretty decent cooling fans, and a hobbed bolt made from hardened steel with best grip [599]. Material is viscous when heated, and has difficulty being pushed into the hotend, a filament warmer that can heat the filament (35–40°C) before it is pushed into the hotend makes it less brittle [599].

Recommended 3D printing conditions for ceramic filament according to Ref. [600] are:

- print temperature: 250–270°C,
- bed temperature: cold,
- print speed: 15–30 mm/s,
- bed adhesion: ABS paint.

Filament is very brittle, warmed to 50°C is more bendable. Another printing tip is that the filament should not rest in hotend at 240°C or higher for 30 min because it will go black and hard. For printing short heat zone and nozzle greater than 0.7 mm is recommended [600].

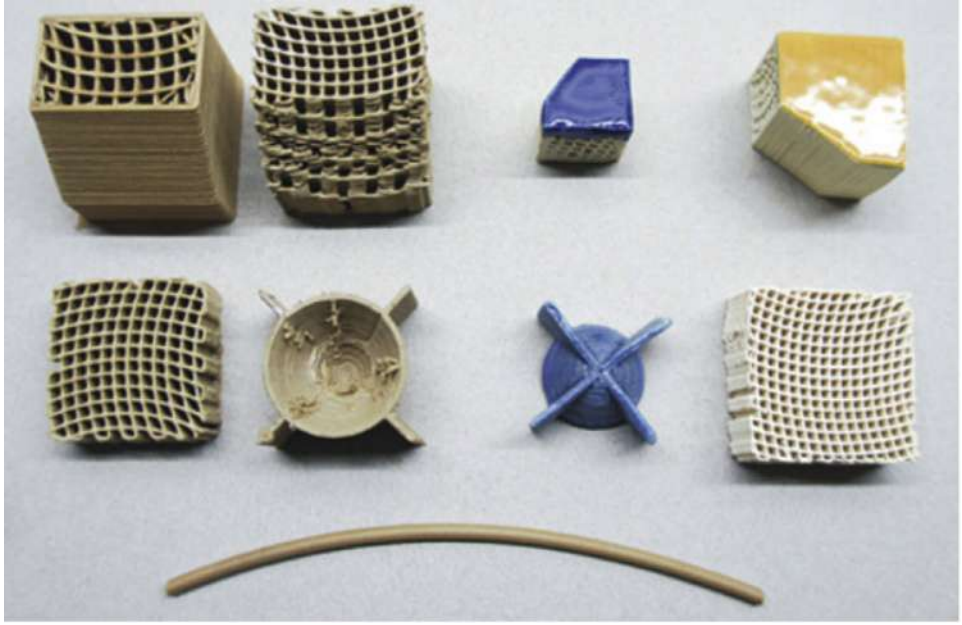


FIGURE 14.28 3D-printed objects from ceramic filament. *From: Bendlay stiff and soft by Lay-Filaments & Kai Parthy.*

Print settings according to Ref. [600] include:

- low number of perimeters (best only 3–4 perimeters),
- do not overlap perimeters more as 15%,
- low percentage of filling between perimeters (<70%),
- do not produce a 100% solid bottom (print meshed filling with max 80%), or 100% filled bottom with only two layers thickness,
- avoiding massive material thickness to reduce occurrence of blows or bubbles,
- printed 3D object must be much smaller than the inlet of kiln for better temperature distribution (while debindering) in kilns chamber,
- layer thickness 0.6–0.8 mm is best for good debindering without blows at surface of printed object.

Sintering can be done in two steps: first 6 h at temperature up to 600°C and in next step 5–10 h at temperature up to 1080°C. 3D-printed object is hard and light gray. In one step sintering, which is done 10 h at temperature up to 1080°C, the 3D-printed object is gray to black [600]. Afterward the printed object is painted with glaze and sintered again at 900°C.

In Fig. 14.28 3D printing object made from ceramic filament from Bendlay stiff and soft by Lay-Filaments & Kai Parthy is shown.

14.5.7 Sandstone filaments

The main benefit of sandstone filaments is that they are a niche product: there is no other filament product in the market right now that can be used to make prints with a stonelike finish. Similar to other composite filaments, sandstone filaments are made by mixing polymer, such as PLA, with a very fine milled chalk. Chalk, also known as limestone or calcium carbonate, is a lightweight and sturdy material that is quite resistant to weathering and can be ground down to a powderlike consistency. Prints made from sandstone filaments simulate the look of sandstone or ceramic, depending on how they are printed and finished [601].

Different surfaces depend on the printing temperature. According to the guidelines for the Laybrick brand of sandstone filaments, printing at around 165°C results in a smoother finish, ceramic look while printing at around 210°C results in a much rougher surface [601]. At higher temperatures, prints come out with a more layered and uneven finish, which also has character and may be desirable for some applications [601].

E.P Smartfil filament for 3D printing is composed of PLA (70%) and ceramic element (30%). Because of its excellent sanding, its excellent print resolution, and its ceramic finish that can be painted, the filament is ideal for users of 3D printing sectors engaged in handicrafts, architecture, odontology, model making, sculpture, etc. [602].

Working with sandstone filament is quite easy since it is less abrasive, does not warp, and performs well over a broad range of printing temperatures. The biggest challenge when working with sandstone filaments is ensuring that the filament does not snap in the middle of the print. The filament itself is quite brittle and can be broken off easily [601].

Recommended 3D printing conditions for sandstone filament according to Ref. [601] are:

- print temperature: 165–210°C,
- bed temperature: not required; 20–50°C if heated,
- print speed: 50–60 mm/s,
- bed adhesion: blue painter's tape,
- cooling fan: recommended,
- enclosure: not required.

To enhance the quality of the colors and add strength the part is coated with a protective layer of epoxy resin (since sandstone parts that are exposed to water will discolor and leave you with a muddy white model). Also, components made from this material are as fragile as porcelain. Allowances for the material's weakness should be made already during the design process [550].

In Table 14.62 printing tips, advantages, and disadvantages of sandstone 3D printing filaments are presented, whereas some typical properties of filaments are given in Table 14.63. In Fig. 14.29 3D printing object made from sandstone filament is shown.

14.5.8 *Wood filaments*

Since 2012, the wood 3D printing filament is available in FDM printing. Printed object looks and feels woodlike, also smells like real wood, though it does not have the same functional properties as the original material. Typically, 3D printing wood filament is composed of around 70% polymer (such as PLA) and 30% wood fibers [606]. Because of the added wood fibers it is more brittle and breaks more easily. First 3D printing wood filaments were made with sawdust, and were more flexible, but the prints looked more like cardboard than wood [606]. Today, several different types of wood filaments, like bamboo, birch, cedar, and many others, are available. Company FormFutura produces seven different wood-based filaments, including those made with birch, cedar, coconut, ebony, olive, pine, and willow, which are made up of 40% wood particles [606].

TABLE 14.62 Advantages and disadvantages of PLA-based sandstone filaments.

	Sandstone filament
PROS	• No plastic feeling • Does not shrink or warp during cooling • Does not require a heated bed • Extremely high interlayer adhesion • Printed objects can be colored and easily grinded • Unique sandstone finish and appearance
CONS	• Not durable and less flexible • Extremely brittle and prone to snapping and breaking • Material is not food safe • Higher wear on printer nozzles
TIPS	• Layer thickness can be from 0.1 to 0.5 mm, though height of lower layer 0.1 mm is not recommended because it could cause possible blockages in the extruder. • Object fill max. 25%, fan needs to be on. • It is recommended to print in rooms with min. 20°C because of filament's brittleness. • The printed object is temperature stable to about 70°C. • Printed object must be hardened (2–4 h), before removing from platform.

Adapted from Refs. [545,603,604].

TABLE 14.63 Properties of 3D printing PLA-based sandstone filament.

	PLA laybrick
Density (g/cm^3)	1.1
Tensile strength: Yield (MPa)	60
Tensile strength: Break (MPa)	11.8
Tensile elongation: Break (%)	8.8
Flexural strength (MPa)	110
Flexural modulus (GPa)	3.9
Notched izod impact (kJ/m^2)	32
Deflection temperature under load: 0.45 MPa (°C)	60
Vicat softening temperature (°C)	70

Adapted from Refs. [603,605].

FIGURE 14.29 3D-printed object from sandstone filament. *From: Bendlay stiff and soft by Lay-Filaments & Kai Parthy.*

The amount of wood fibers in polymer matrix can vary. The effect of wood content (10%−50%) in composite PLA filaments on the properties of 3D printed objects was investigated by Kariz et al. [607]. They found out that the density of the filaments and 3D-printed objects slightly decreased with increasing wood content. The tensile strength slightly increased at filament containing 10% wood fibers, but with the higher levels of wood content decreased, considerably. With increasing wood content the surface became rougher, more voids and visible clusters of wood particles were also present [607]. In other research [608] the viability of using furniture waste, as recycled wood waste powder, as a filler for 3D printing PLA filament, was investigated. By mixing PLA pellets and recycled wood waste powder, a filament was produced with a diameter size of 1.65 mm. Study has demonstrated a technically viable methodology of upcycling furniture wood waste into useable 3D printable furniture components [608].

The shade of brown in wood filament can be controlled by setting the extrusion temperature. While 3D printing at lower temperatures will give a very light shade, high temperatures will result in a strong, dark brown because at higher temperatures wood fibers start to burn, creating darker shades. With varying the print temperature annual rings in print can be simulated, too [550].

Printed objects can be sanded, grinded, and painted like standard wooden products. 3D printing material can be very aesthetically appealing. Today, wood filaments are often used for decors or materials with a wooden nature to replace wood (cups, wooden box, wooden figurine, or the likes) [609].

TABLE 14.64 Advantages and disadvantages of PLA-based wood filaments.

	Wood filament
PROS	• Versatility • Durability • Produce different shades of brown wooden-like surfaces • Easy postprocess, like cut, grind, and paint • Very good interlayer adhesion
CONS	• Softer and weaker compared to PLA • Reduced flexibility and tensile strength • It can break easily • Stringing possible depending on print • Not suitable for utensils
TIPS	• A special attention is needed when filament is fed into the extruder. • To prevent dry extrusion increasing printing speed is recommended. • For smoother prints, staying in the 190–220°C range is recommended. • To avoid stucking the filament in the heat chamber or in the nozzle, a 0.5 mm nozzle or larger is recommended. • Prone to clogging – purging after printing to keep the nozzle clean.

Adapted from Refs. [545,609].

Printing filament filled with wood fibers is similar to printing unfilled filament. For PLA wood composite the recommended printing temperature range is set between 175 and 250°C [609]. As wood is highly flammable the caution at printing is necessary. If the hotend is too hot and the filament is not extruded fast enough, the print could become damaged or even catch fire [606]. During printing, it basically smells like burning wood. A proper ventilation is needed. To prevent clogging, a nozzle larger than the standard 0.4 mm is recommended. A heated bed is not needed necessary, though it is recommended to obtain high-quality prints [606]. Wood 3D-printed object is not polishable like ABS. Sanding with fine grid sandpaper and then applying lacquer give the satisfactory finish.

Recommended 3D printing conditions for wood PLA-based filament according to Ref. [610] are:

- print temperature: 200–220°C,
- bed temperature: not required; 60–70°C if heated,
- print speed: 40–70 mm/s,
- bed adhesion: PI tape, hairspray,
- cooling fan: recommended at high settings.

In Table 14.64 printing tips, advantages, and disadvantages of 3D printing wood filaments are presented, whereas some typical properties of filaments are given in Table 14.65. In Fig. 14.30 3D-printed objects made from composite PHA/PLA filament reinforced with bamboo and from cork filled filament are shown.

14.5.9 Special filaments

The field of 3D printing material improvements is one of the most interesting domains in 3D printing, as new developments are made constantly. 3D printing grows more sophisticated every day. The technology is capable of producing items that have special shape or appearance [614]. Some of special filaments are shown in Fig. 14.31.

14.5.9.1 Translucent/transparent filament

BendLay is an exciting filament, a modified butadiene that is extremely translucent, 91% of light passes through (Fig. 14.31A). It is clear like PC and also is quite flexible. It is high-impact resistant and nearly unbreakable, and with a shore hardness of D65 is bendable up to 175% [609]. Compared to ABS, it shows a lot less warping and has high interlayer adhesion, making it quite easy to print with. Recommended print temperatures are between 215 and 240°C. BendLay will keep its flexability if it is not printed with a too thick wall. It is best used where ABS is too hard and where flexible PLA is too soft, and is ideal for flex prints. BendLay sticks very well to ABS and PLA, so it is suitable for multimaterial prints [609].

Recommended 3D printing conditions for BendLay filament according to Ref. [615] are:

- print temperature: 235°C,
- bed temperature: not required; 20–40°C if heated,

TABLE 14.65 Properties of 3D printing PLA-based wood filaments.

	Wood	Bamboo	Cork
Density (g/cm^3)	1.15	1.15	1.18
Melt flow index (g/10 min)	4–7.5	4–7.5	3–5
Tensile strength: Yield (MPa)	46	46	40
Tensile strength: Break (MPa)	42	36	29
Tensile elongation: Yield (%)	4.8	5	5
Tensile elongation: Break (%)	5.5	8	11
Tensile modulus (GPa)	3.29	3.3	2.47
Flexural strength (MPa)	70	70	
Flexural modulus (GPa)	3.93	3.6	2.49
Charpy notched impact strength (kJ/m^2)	4.2	3	4
Vicat softening temperature: 0.45 MPa (°C)			60
Melting temperature (°C)	>155	>155	>155

Adapted from Refs. [611–613].

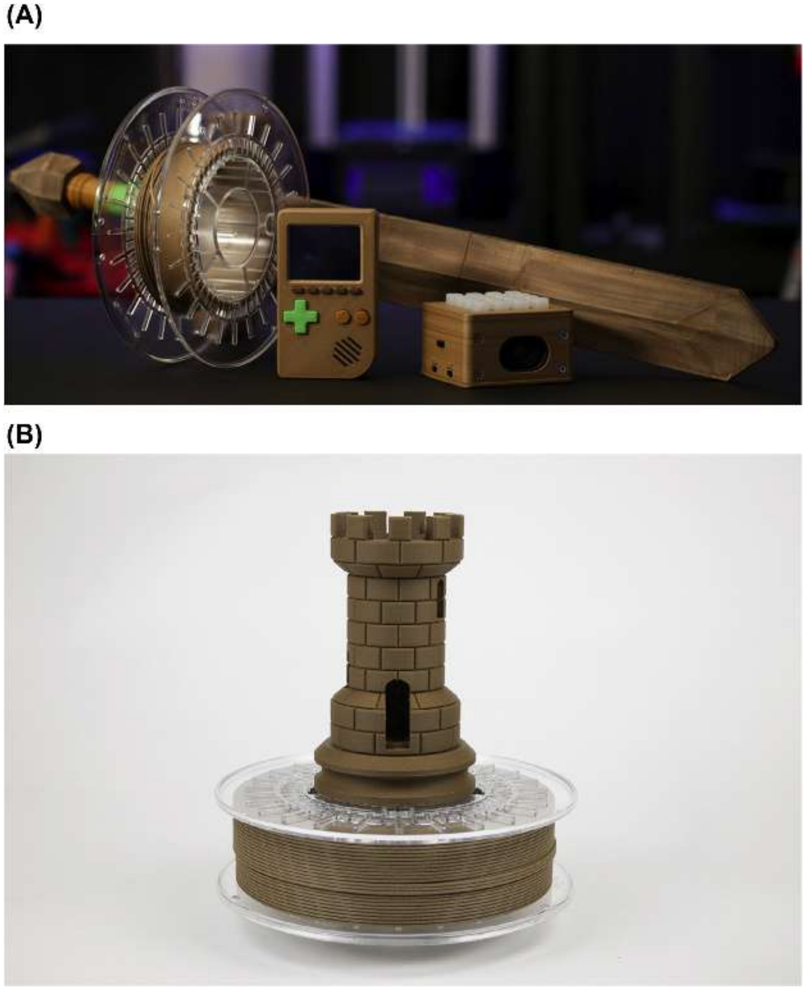


FIGURE 14.30 3D-printed objects from: (A) bamboo wood filament, (B) cork filament. *(A) Image credits: Adafruit Industries LLC. (B) From: Schaaktoren "Rook" by Seechless: http://www.thingiverse.com/thing:99028 Image with spool by: colorFabb.*

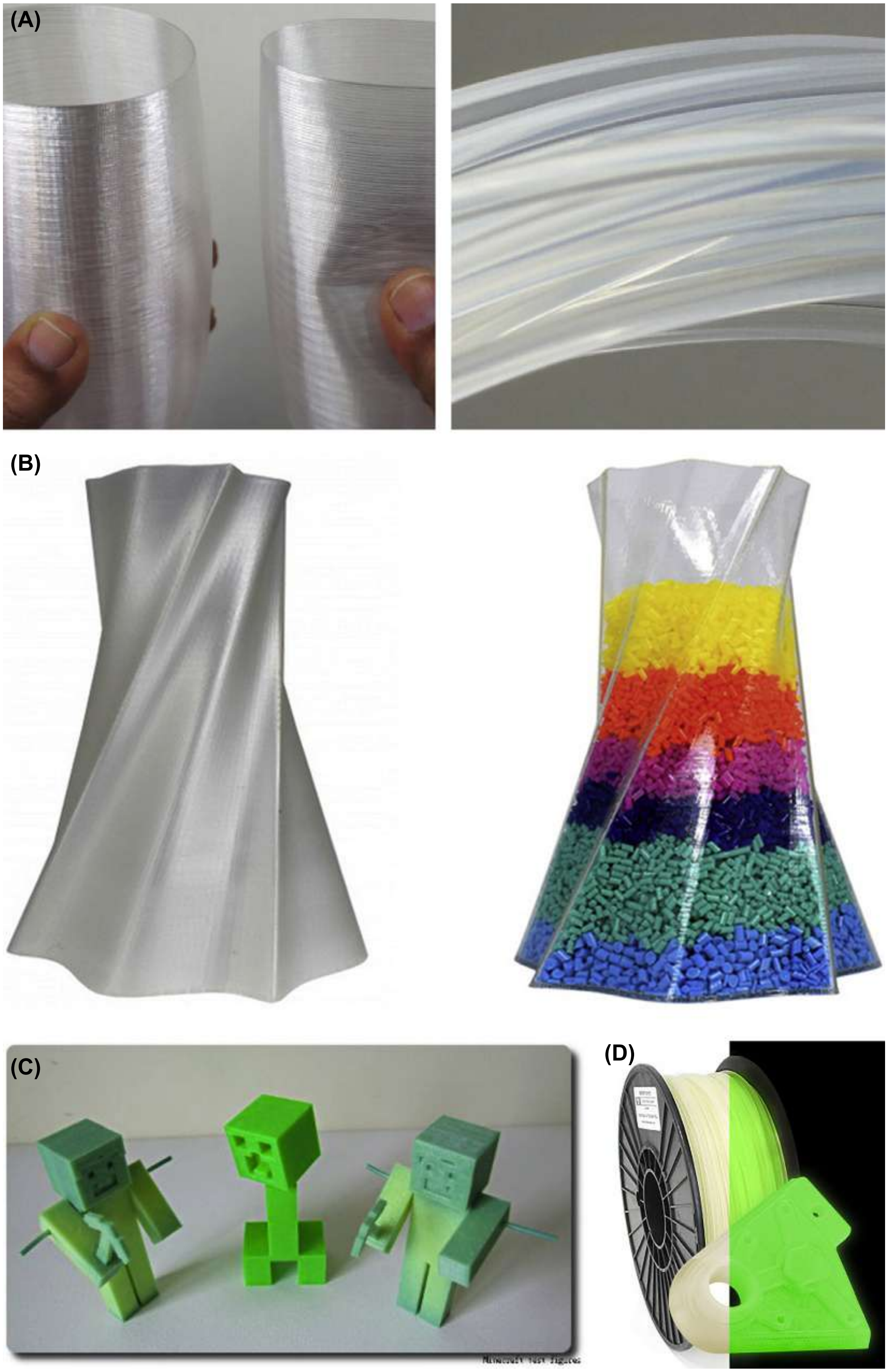


FIGURE 14.31 3D-printed objects from special 3D printing filaments: (A) translucent, (B) glace, (C) color changing, (D) glow in the dark. *(A) From: Bendlay stiff and soft by Lay-Filaments & Kai Parthy; (B) Image credits: Smart Materials 3D printing; (C) Image credits: 3D FilaPrint; (D) Image credits: MatterHackers Inc.*

- print speed: 50 mm/s,
- cooling fan: not recommended,
- enclosure: not necessary.

Transparent printing using an FDM 3D printer is a challenging process, where printing conditions must be precise adjusted to minimize light refraction of printed object. Adjustments include extrusion temperature and flow rate, print bed temperature, printing speed, layer height thickness, and nozzle diameter [616]. Clear 3D printing filaments are made from different polymers, such as PLA, ABS, PMMA, PC, and PETG. However, PLA filaments usually have a slight yellowish tinge, ABS is translucent rather than transparent, PMMA and PC are rather clearly compared to others, whereas PETG is the clearest 3D printing filament available [616].

14.5.9.2 Glace filament

Glace filament produced by Smart Materials 3D is a material with glace effect with high transparency (Fig.14.31B). It is produced from polyvinyl butyral, which is prepared from PVA by reaction with butyraldehyde. It has better mechanical properties than ABS and PLA, good impact resistance, and high flexibility [617]. It is easy to print without warping. A chemical polish with alcohol can be applied, resulting in a completely smooth surface finish. Additionally, a greater adhesion in between layers results in higher strength. By polishing with alcohol in thin profiles, pieces of high transparency that simulate crystal are obtained [617]. Printed object can be immersed into alcohol or the evaporation method by introducing a paper impregnated with alcohol around the piece in a container can be used [618].

Recommended 3D printing conditions for Glace filament according to Ref. [619] are:

- print temperature: 220 ± 15°C,
- bed temperature: not required; 0–70°C if heated,
- cooling fan: recommended at high settings.

14.5.9.3 Rainbow/multicolor filament

Multicolor filaments have been developed for multicolor prints using a single extruder (3D printer with one nozzle). This makes multicolor printing as easy as single-color prints. Because there are several colors on one spool consecutively, the prints will consist of several colors automatically. It is PLA based, and contains the same features as standard PLA and same printing settings [620].

14.5.9.4 Color changing filament

3D-printed material changes color in response to light or temperature. It is an interesting property that can increase the functional capabilities of 3D-printed devices for industries like electronics, health care, and quantum computing [614].

Filament reacts by changing its color when exposed to the temperature (Fig. 14.31C). There are different colors possible. At Reprapper Tech PLA Blue Green to Yellow Green Thermochanging filament the color at low temperature is green and as the temperature increases the filament turns yellow and when it cools goes back to green. The temperature change filaments from RepRapper are gray to white, green to yellow, purple to pink, white to blue, and orange to yellow. Depending on the activation temperature the color can change just by holding the printed object in warm hand. The change of color is triggered also by UV light. When printed object is exposed to the sun or ultraviolet's radiation it absorbs the sunlight/UV energy and produces the color change, colorless turns to colored [621,622]. The UV light color changing filament available from Matterhackers and RepRapper are: white to purple, white to red, natural to blue, and natural to purple [623]. Color changing filaments are PLA or ABS based and have similar properties and printing settings as pure PLA or ABS.

In recent research 3D-printed functional devices with reversible photochromism were obtained based on the unique photo and redox properties of nanostructured polyoxometalates [624]. The researchers developed a photoactive molecule that changes from colorless to blue when exposed to light. The color change can then be reversed by exposure to oxygen. They then 3D printed composite materials by combining the photoactive molecules with a custom-made polymer, creating a material that can store material reversibly – in a way, it is like 3D printed invisible ink [614].

Another color changing 3D printable filament is Glow in the dark filament (Fig. 14.31D). It is designed to glow brightly for an extended amount of time. However, you need to charge the object or expose it to a light source to allow it to emit light [545]. When exposed to light for around 15 min material reciprocates by glowing in the dark with an eerily blue or green shade [625]. It can be used for caution signs, novelty items, toys, wearables, phone cases, or decorative products [545]. It is PLA or ABS based, and as such is similar to the standard PLA or ABS.

14.6 Final considerations

AM is predicted to be at the forefront of the fourth industrial revolution, already exhibiting tremendous growth for 3D printing products and services on the worldwide market. 3D printing industry is expected to grow at a compound annual growth rate of 26.4% between 2020 and 2024 [626]. Besides enhanced 3D-printed product quality, improved efficiency and lower costs are the main drivers. Fast prototyping, freedom of design, mass customization, the ability to manufacture complex structures, and waste minimization are the main benefits of 3D printing [3]. Thermoplastics used in FDM are readily available, inexpensive materials with very diverse properties, making the FDM process affordable, easy, and safe to operate 3D printing technique for making a broad range of products, from household items to sophisticated objects in health care, civil engineering, and various industrial applications.

In this chapter an overview of thermoplastic polymers used in FDM printing is given, including representatives from all three groups of the pyramid of polymers classification. Engineering thermoplastics are the most used 3D printing filaments with a vast variety of properties, like flexibility, stiffness, toughness, rigidity, enhance strength, impact resistance, good wear resistance, heat, abrasion, and chemical resistance. Among commodity and engineering polymers the most flexible are PP, PA, and TPU/TPE, later being also elastic and soft. The highest impact resistance shows ABS, ASA, PC, PA, PP, whereas the strength PC, PA, and PES. The most of them have high durability; only PP, PLA, and PVA are less durable. PP and PETG are known for their high water and chemical resistance, whereas HIPS and PVA are dissolvable, PVA also in water. Most of them are also heat resistant, with exception of PLA, PVA, PMMA, and TPU/TPE. High-performance polymers are used to fabricate objects with outstanding thermal, chemical, and weathering resistance, superior strength, and other mechanical properties at excellent strength-to-weight ratios. They are used to produce strong and durable objects for highly demanding application. Some of 3D printing filaments are biocompatible, suitable for sterilization or approved as food contact materials, which broadens their use into the field of dental, medical, and food contact applications. Polymer composites obtained with addition of fibers or particles into the polymeric matrix result in improved mechanical properties and wear resistance of printed objects or they obtain special features, such as magnetic, conductive, color changing. Metal, ceramic, sandstone, and wood composites attain the properties of added fiber and look like a metal, ceramic, or wood object at maintaining the favorable characteristics of polymeric matrix. In Table 14.66 printability and main features of mostly used commercial 3D printing filaments are summarized.

TABLE 14.66 Printability, service temperature, and special properties of selected 3D printing filaments.

	Printability	Service temperature	Special properties
PP	Low (2/5)	100°C	Flexible, water and chemical resistant
MPPA	Good (4/5)	70–90°C	Rigid, transparent, clear
HIPS	Medium (3/5)	100°C	Dissolvable, impact resistant
PVA	Low (2/5)	75°C	Dissolvable, water soluble, biodegradable
ABS	Medium (3/5)	98°C	Durable, impact resistant
ASA	Medium (3/5)	95°C	Durable, impact resistant, UV resistant
PLA	Very good (5/5)	52°C	Biodegradable, stiff
PA	Medium (3/5)	80–95°C	Durable, strong, flexible, fatigue resistant
PETG	Good (4/5)	73°C	Durable, flexible, fatigue resistant
PC	Medium (3/5)	121°C	Durable, strong, tough, heat resistant
TPU	Medium (3/5)	60–74°C	Extremely flexible, abrasion resistant
PEI	Low (2/5)	150–175°C	Durable, high strength, high heat resistant, high chemical resistant
PEEK	Low (2/5)[a]	250°C	Durable, exceptional hard, stiff, strong, creep resistant
PEKK	Low (2/5)[a]	150°C	Durable, exceptional thermal, chemical, and mechanical properties
PPSU	Low (2/5)[a]	180–200°C	Durable, rigid, tough, heat and chemical resistant

[a] *Challenging, high-temperature printer needed.*

Adapted from Refs. [290,441,627–631].

Choosing the right polymer and processing conditions is critical to get the desired properties for a 3D-printed item. PLA is one of the easiest polymers to 3D print, is stiff, and provides good visual quality. ABS is preferred when higher toughness and temperature resistance is required. ASA with the similar properties as ABS and excellent weathering resistance is used for outdoor applications. Compared to PLA they both have lower printability. PETG and PA are 3D printing materials with good mechanical properties and durability, and PC is among engineering polymers the strongest material and can replace ABS in more demanding applications. PETG and other PESs are easier to 3D print than PA, PC, or TPU, though compared to PLA they all have lower visual quality and printability. All high-performance polymers have superior properties, but are more difficult and challenging to print, PEKK exhibiting better printability than PEI and PEEK.

Properties improvement of 3D printing filaments and development of new materials is one of the most important areas for innovations in 3D printing. Focus is shifting toward the functionality of the printed object, and in development of new composites that are compatible with the available printers and able to satisfy the needs for special applications.

References

[1] B.N. Turner, R. Strong, S.A. Gold, A review of melt extrusion additive manufacturing processes: I, Proc. Des. Model. Rapid Prototyp. J. 20 (3) (2014) 192–204, https://doi.org/10.1108/RPJ-01-2013-0012.
[2] J.R.C. Dizon, A.H. Espera, Q. Chen, R.C. Advincula, Mechanical characterization of 3D-printed polymers, Adit. Manuf. 20 (2018) 44–67, https://doi.org/10.1016/j.addma.2017.12.002.
[3] T.D. Ngo, A. Kashani, G. Imbalzano, K.T.Q. Nguyen, D. Hui, Additive manufacturing (3D printing): a review of materials, methods, applications and challenges, Compos. B Eng. 143 (2018) 172–196, https://doi.org/10.1016/j.compositesb.2018.02.012.
[4] S.C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, Polymers for 3D printing and customized additive manufacturing, Chem. Rev. 117 (2017) 10212–10290, https://doi.org/10.1021/acs.chemrev.7b00074.
[5] E.J. Hunt, C.L. Zhang, N. Anzalone, J.M. Pearce, Polymer recycling codes for distributed manufacturing with 3-D printers, Resources, Conserv. Recycl. 97 (2015) 24–30, https://doi.org/10.1016/j.resconrec.2015.02.004.
[6] J.W. Stansbury, M.J. Idacavage, 3D printing with polymers: challenges among expanding options and opportunities, Dent. Mater. 32 (1) (2016) 54–64, https://doi.org/10.1016/j.dental.2015.09.018.
[7] B.T. Wittbrodt, A.G. Glover, J. Laureto, G.C. Anzalone, D. Oppliger, J.L. Irwin, J.M. Pearce, Life-cycle economic analysis of distributed manufacturing with open-source 3-D printers, Mechatronics 23 (6) (2013) 713–726, https://doi.org/10.1016/j.mechatronics.2013.06.002.
[8] M. Hofmann, 3D printing gets a boost and opportunities with polymer materials, ACS Macro Lett. 3 (2014) 382–386, https://doi.org/10.1021/mz4006556.
[9] M. Fahad, P. Dickens, M. Gilbert, Novel polymeric support materials for jetting based additive manufacturing processes, Rapid Prototyp. J. 19 (4) (2013) 230–239, https://doi.org/10.1108/13552541311323245.
[10] W. Posch, Polyolefins, in: M. Kutz (Ed.), Applied Plastics Engineering Handbook, Elsevier, Amsterdam, 2011, pp. 23–48.
[11] Polyolefins, MaterialMagazin, (2019). http://www.materialmagazin.com/index.php/kunststoffe/polyolefine-pe-pp-und-pmp. (Accessed 17 December 2018).
[12] H. von Pechmann, Ueber Diazomethan und Nitrosoacylamine, Ber. Dtsch. Chem. Ges. 31 (3) (1898) 2640–2646, https://doi.org/10.1002/cber.18980310314.
[13] K. Harrison, Polyethene, 3DChem.com - chemistry, Struct. 3D Mol. (2007). http://www.3dchem.com/Polyethylene.asp (Accessed 25 November 2018).
[14] M.P. McDaniel, Review of Phillips chromium catalyst for ethylene polymerization, in: R. Hoff, R.T. Mathers (Eds.), Handbook of Transition Metal Polymerization Catalysts, John Wiley & Sons, Hoboken NJ, 2009 (Chapter 10).
[15] W. Reusch, Polymers, 2013. https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/polymers.htm (Accessed 17 December 2018).
[16] D. Feldman, Polymer history, Des. Monomers Polym. 11 (1) (2008) 1–15, https://doi.org/10.1163/156855508X292383.
[17] K.B. Triebel, B.E. Hauger, D.E. Parsons, L.H. Carver, K.M. Powell, F.K. Wood-Black, Discovery of Polypropylene and Development of High Density Polyethylene, American Chemical Society, 1999, pp. 1–5.
[18] G.B. Kauffman, Polymer pioneers: a popular history of the science and technology of large molecules (Morris, Peter J.T.), J. Chem. Educ. 65 (11) (1988) A301, https://doi.org/10.1021/ed065pA301.2.
[19] J.A. Brydson, Plastics Materials, sixth ed., Butterworth Heinemann, London, 1995 (Chapter 1).
[20] W. Kaminsky, The discovery of metallocene catalysts and their present state of the art, J. Polym. Sci. Polym. Chem. 42 (16) (2004) 3911–3921, https://doi.org/10.1002/pola.20292.
[21] K.S. Whiteley, G.T. Heggs, H. Koch, R.L. Mawer, W. Immel, Polyolefins, in: Ullmann's Encyclopedia of Industrial Chemistry, vol. 28, Wiley-VCH, Weinheim, 2003, p. p.393.
[22] R.G. Jones, J. Kahovec, R. Stepto, E.S. Wilks, M. Hess, T. Kitayama, W.V. Metanomski (Eds.), Compendium of Polymer Terminology and Nomenclature: IUPAC Recommendations 2008, RCS Publishing, 2009.
[23] Polyethylene, PolymerProcessing.com. http://www.polymerprocessing.com/polymers/PE.html. (Accessed 10 December 2018).
[24] Polypropylene, Encyclopædia Britannica, 2019. https://www.britannica.com/science/polypropylene (Accessed 10 December 2018).
[25] Propylene. PubChem, National Institutes of Health. https://pubchem.ncbi.nlm.nih.gov/compound/Propylene#section=Computed-Descriptors. (Accessed 10 December 2018).
[26] Poly(ethene) (Polyethylene), the Essential Chemical Industry-Online, CIEC University of York, 2017. http://www.essentialchemicalindustry.org/polymers/polyethene.html (Accessed 10 December 2018).

[27] Polyethylene - high density (HDPE), Production and Manufacturing Process ICIS, 2010, in: https://www.icis.com/explore/resources/news/2007/11/06/9076153/polyethylene-high-density-hdpe-production-and-manufacturing-process/ (Accessed 11 December 2018).

[28] Polypropylene, PSLC University of Southern Mississippi. https://pslc.ws/macrog/pp.htm. (Accessed 11 December 2018).

[29] C. Hindle, Polypropylene, British Plastic Federation, 2019. http://www.bpf.co.uk/plastipedia/polymers/pp.aspx (Accessed 17 December 2018).

[30] V.T. Ponomareva, N.N. Likhacheva, Production of plastics based on metallocene catalysts, Plast. Massy 4 (2001) 8—11, https://doi.org/10.1177/0307174X0202900203.

[31] M. Gahleitner, C. Paulik, Polypropylene, in: Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2014, pp. 1—44.

[32] PP — Polypropylene — Manufacturing process of PP (Polypropylene), Guichon Valves. http://guichon-valves.com/faqs/pp-polypropylene-manufacturing-process-of-pp-polypropylene/. (Accessed 17 December 2018).

[33] Polyolefins (Polyalkenes), Polymer Properties Database, CROW, 2015. https://polymerdatabase.com/polymer%20classes/Polyolefin%20type.html (Accessed 16 December 2018).

[34] Polyethylene (High Density) HDPE, British Plastic Federation. https://www.bpf.co.uk/plastipedia/polymers/hdpe.aspx. (Accessed 13 December 2018).

[35] Polyethylene Injection Molding, Charloma. http://www.charloma.com/polyethylene-injection-molding.html. (Accessed 17 December 2018).

[36] Polypropylene Processing Guide, INEOS Olefins & Polymers USA. https://www.ineos.com/globalassets/ineos-group/businesses/ineos-olefins-and-polymers-usa/products/technical-information—patents/ineos_polypropylene_processing_guide.pdf. (Accessed 15 December 2018).

[37] A Guide to Polyolefin Film Extrusion, LyondellBasell. https://www.lyondellbasell.com/globalassets/documents/polymers-technical-literature/A_Guide_to_Polyolefin_Film_Extrusion.pdf. (Accessed 16 December 2018).

[38] Polypropylene (PP) Plastic - Complete Guide, Omnexus. https://omnexus.specialchem.com/selection-guide/polypropylene-pp-plastic#-Properties. (Accessed 13 December 2018).

[39] High Density Polyethylene (HDPE), RTP Company. https://www.rtpcompany.com/products/product-guide/high-density-polyethylene-hdpe/. (Accessed 14 December 2018).

[40] HDPE (High Density Polyethylene) United Plastic Components. http://www.upcinc.com/resources/materials/HDPE.html. (Accessed 14 December 2018).

[41] Polypropylene - is it different from polyethylene? Glob. Plastic Sheet. (2016). https://www.globalplasticsheeting.com/our-blog-resource-library/bid/92169/polypropylene-is-it-different-from-polyethylene (Accessed 14 December 2018).

[42] High Density Polyethylene — HDPE, AZO Materials, 2001. https://www.azom.com/article.aspx?ArticleID=421 (Accessed 20 December 2018).

[43] Polyolefin Plastic, UL Prospector. https://plastics.ulprospector.com/generics/38/polyolefin. (Accessed 20 December 2018).

[44] Polyethylene (PE) Typical Properties Generic HDPE, UL Prospector. https://plastics.ulprospector.com/generics/27/c/t/polyethylene-pe-properties-processing/sp/5. (Accessed 20 December 2018).

[45] Polypropylene (PP) Typical Properties Generic PP Homopolymer, UL Prospector. https://plastics.ulprospector.com/generics/39/c/t/polypropylene-pp-properties-processing/sp/11. (Accessed 20 December 2018).

[46] Tips for Injection Molding INEOS O&P HDPE Resins, INEOS Olefins & Polymers USA, 2008. https://www.ineos.com/globalassets/ineos-group/businesses/ineos-olefins-and-polymers-usa/products/technical-information—patents/tips_for_injection_molding_ineos_hdpe_resins.pdf (Accessed 19 December 2018).

[47] H.F. Giles, J.R. Wagner, E.M. Mount, Extrusion: the Definitive processing Guide and Handbook, William Andrew Inc., Norwich, NY, 2005.

[48] Extrusion processing guide: PE-HD — high-density polyethylene, Plastics.gl (2015), in: https://www.plastics.gl/extrusion-profile/extrusion-processing-guide-pe-hd-high-density-polyethylene/ (Accessed 19 December 2018).

[49] Extrusion processing guide: PP — polypropylene, Plastics.gl (2015), in: https://www.plastics.gl/extrusion-profile/extrusion-processing-guide-pp-polypropylene/ (Accessed 17.12.2018).

[50] Polypropylene Injection Molding, Charloma. http://www.charloma.com/polypropylene-injection-molding.html. (Accessed 19 December 2018).

[51] HDPE (High-Density Polyethylene), Retlaw Industries. http://www.retlawindustries.com/PlasticTypes/HDPE. (Accessed 20 December 2018).

[52] C. Maier, T. Calafut, Polypropylene: The Definitive User's Guide and Databook, William Andrew Inc., Norwich, NY, 1998.

[53] G.P. Thomas, Recycling of high-density polyethylene (HDPE or PEHD), AZO Cleantech (2012). https://www.azocleantech.com/article.aspx?ArticleID=255 (Accessed 10 January 2019).

[54] APR Design® Guide for Plastics Recyclability for High Density Polyethylene, Association of Plastic Recyclers, 2018. https://www.plasticsrecycling.org/images/pdf/design-guide/HDPE_APR_Design_Guide.pdf (Accessed 10 January 2019).

[55] F.P. La Mantia, Recycling of polypropylene, in: J. Karger-Kocsis (Ed.), Polypropylene: An A-Z Reference, Kluwer Academic Publishers, Dordrecht, 1999, pp. 701—705.

[56] APR Design® Guide for Plastics Recyclability for Polypropylene, Association of Plastic Recyclers, 2018. https://www.plasticsrecycling.org/images/pdf/design-guide/PP_APR_Design_Guide.pdf (Accessed 10 January 2019).

[57] G.P. Thomas, Recycling of polypropylene (PP), AZO Cleantech (2012). https://www.azocleantech.com/article.aspx?ArticleID=240 (Accessed 12 January 2019).

[58] C. Goldsberry, Scientific tests prove HDPE can be recycled at least 10 times, Plast. Today (2018). https://www.plasticstoday.com/packaging/scientific-tests-prove-hdpe-can-be-recycled-least-10-times/68825031358152 (Accessed 12 January 2019).

[59] R. Leblanc, An overview of polypropylene recycling, Balance (2019). https://www.thebalancesmb.com/an-overview-of-polypropylene-recycling-2877863 (Accessed 14 January 2019).

[60] S. Rohringer, 2019 3D printer filament guide — all you need to know, All3DP.com (2019). https://all3dp.com/1/3d-printer-filament-types-3d-printing-3d-filament/ (Accessed 17.7.2019).

[61] HDPE Filament for your 3D printer, Filaments Directory, 2015–2019. https://www.filaments.directory/en/plastics/hdpe. (Accessed 17 July 2019).

[62] M. Griffin, HDPE (3D printing material) – all you need to know, All3DP.com (2019). https://all3dp.com/2/hdpe-3d-printing-material-all-you-need-to-know/ (Accessed 18 August 2019).

[63] Polypropylene. Simplify3D. https://www.simplify3d.com/support/materials-guide/polypropylene/. (Accessed 15 January 2019).

[64] R. Baguley, 3D printing materials: the pros and cons of each type, Tom's Guide (2017). https://www.tomsguide.com/us/3d-printing-materials,news-24392.html (Accessed 18 August 2019).

[65] 3D printer filament comparison guide, MatterHackers. https://www.matterhackers.com/3d-printer-filament-compare. (Accessed 10 July 2019).

[66] 3D Printing with Polypropylene, Leapfrog 3D Printers. https://www.lpfrg.com/en/3d-printing-polypropylene/. (Accessed 11 December 2018).

[67] Technical Data Sheet PP, Ultimaker, 2018. https://ultimaker.com/download/74977/UM180821%20TDS%20PP%20RB%20V11.pdf (Accessed 10 December 2018).

[68] L. Henri, Thermohygroelastic Properties of Polymethylmethacrylate, PR-TN 2007/00440, Koninklijke Philips Electronics NV, 2007, pp. 11–13.

[69] Poly(methyl Methacrylate), Chemical Book, 2018. https://www.chemicalbook.com/ChemicalProductProperty_EN_CB1221699.htm (Accessed 18 February 2019).

[70] Poly(methyl Methacrylate), Merck, 2019. https://www.sigmaaldrich.com/catalog/product/sial/81489?lang=en&region=SI (Accessed 16 March 2019).

[71] G. Odian, Principles of Polymerization, fourth ed., John Wiley & Sons, Hoboken, NJ, 2004, pp. 198–235.

[72] M. Stickler, T. Rhein, Polymethacrylates, in: B. Elvers, S. Hawkins, G. Schultz (Eds.), Ullmann's Encyclopedia of Industrial Chemistry A21, VHS, New York, 1992, p. 473.

[73] J. Vanderbergh, Y. Junkers, Polyacrylates, in: O. Olabisi, K. Adewale (Eds.), Handbook of Thermoplastics, CRC Press, Boca Raton FL, 2016 (Chapter 5).

[74] B.B. Kine, R.W. Novak, Acrylic and methacrylic ester polymers, in: J.I. Kroschwitz, H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges (Eds.), Encyclopedia of Polymer Science and Engineering, vol. 1, John Wiley & Sons, Chicester, 1985, p. 262.

[75] How do you recycle acrylic resin? AZO Mater. (2012). https://www.azom.com/article.aspx?ArticleID=7945 (Accessed 28 February 2019).

[76] Poly(methyl methacrylate) PMMA, Steinwall. https://www.steinwall.com/wp-content/uploads/2016/05/Polymethyl-methacrylate-PMMA.pdf. (Accessed 18 December 2018).

[77] Poly(methyl methacrylate) PMMA, Milton Plastics. http://www.miltonplastics.com/index.php/Picture/show/2.html. (Accessed 11 January 2019).

[78] Acrylic Used in Plastic Injection Molding, Retlaw Industries. http://www.retlawindustries.com/PlasticTypes/Acrylic. (Accessed 19 December 2018).

[79] Acrylics, International Polymer Solutions. https://www.ipolymer.com/pdf/Acrylic.pdf. (Accessed 19 December 2018).

[80] Polymethacrylates, Polymer Properties Database, CREW, (2015). http://polymerdatabase.com/polymer%20classes/Polymethacrylate%20type.html. (Accessed 19 December 2018).

[81] PMMA or Acrylic: Guide to Support Your Future 'Transparent' Developments, Omnexus. https://omnexus.specialchem.com/selection-guide/polymethyl-methacrylate-pmma-acrylic-plastic. (Accessed 1 July 2019).

[82] Everything You Need To Know About Acrylic (PMMA), Creative Mechanisms, (2016). https://www.creativemechanisms.com/blog/injection-mold-3d-print-cnc-acrylic-plastic-pmma. (Accessed 1 July 2019).

[83] G. Beall, B. Design, Designing with acrylic, Plast. Today (2003). https://www.plasticstoday.com/content/design-designing-acrylic/9621041932489 (Accessed 1 July 2019).

[84] Polymethyl Methacrylate - PMMA (Acrylic), Tangram Technology, 2015. http://www.tangram.co.uk/TI-Polymer-PMMA.html#GP (Accessed 2 February 2019).

[85] Methyl Methacrylate (MM) Typical Properties Generic MABS, UL Prospector. https://plastics.ulprospector.com/generics/21/c/t/methyl-methacrylate-mm-properties-processing. (Accessed 2 February 2019).

[86] Acrylic resins: injection molding guide, Altuglas Int. (2013). https://www.altuglas.com/export/sites/altuglas/.content/medias/downloads/literature/injection-molding-guide-for-medical-grades.pdf (Accessed 2 February 2019).

[87] Extrusion processing guide: PMMA – polymethylmethacrylate, Plastics.gl (2015), in: https://www.plastics.gl/extrusion-profile/extrusion-processing-guide-pmma-polymethylmethacrylate/ (Accessed 15 January 2019).

[88] PMMA/Acrylic Sustainable Solutions, Properties and Benefits, The Methacrylate Sector Group, pmma-online.eu. https://www.pmma-online.eu/pmma-science/properties-and-benefits/. (Accessed 15 January 2019).

[89] How do you recycle acrylic resin? AZO Mater. (2012). https://www.azom.com/article.aspx?ArticleID=7945 (Accessed 17 February 2019).

[90] PMMA/Acrylic Sustainable Solutions, Sustainability, The Methacrylate Sector Group. pmma-online.eu. https://www.pmma-online.eu/sustainability/. (Accessed 15 February 2019).

[91] E. Tyson, Why You Should Try PMMA Filament – and How to Print it, 2017. https://rigid.ink/blogs/news/why-you-should-try-pmma-filament-and-how-to-print-it (Accessed 17 December 2018).

[92] PMMA 3D Printer Filament. rigid.ink. https://rigid.ink/products/pmma-1-75-mm-0-03-mm-tolerance. (Accessed 23 December 2018).

[93] The 3D Printing Acrylic Filament, TreeD Filaments. http://treedfilaments.com/3d-printing-filaments/transparent-methacrylate-hirma/. (Accessed 23 December 2018).

[94] PMMA (polymethyl methacrylate) Material, Vexma Technologies. http://vexmatech.com/pmma-3dprinting-material.html. (Accessed 22 December 2018).

[95] PMMA Filament for your 3D printer, Filaments Directory. https://www.filaments.directory/en/plastics/pmma. (Accessed 22 January 2018).

[96] PMMA Technical Data Sheet. https://cdn.shopify.com/s/files/1/0714/6487/files/rigid.ink-PMMA-TDS.pdf. (Accessed 10 January 2019).

[97] pmma filament. https://www.filament-pm.com/stranka/.../75/technical-data-sheets-32. (Accessed 10 January 2019).

[98] W.C. Teach, G.C. Kiessling, Polystyrene, Reinhold Publishing Corporation, New York, 1960 (Chapter 4).

[99] C.A. Russell, S.A.H. Wilmot, V. Campbell, N.G. Coley, Chemistry, society, and environment: a new history of British chemical industry, R. Soc. Chem., Cambridge (2000) 239—269.

[100] J.A. Brydson, Plastic Materials, fifth ed., Butterworth-Heinemann, London, 1989 (Chapter 1).

[101] C.A. Brighton, G. Pritchard, G.A. Skinner, Styrene Polymers: Technology and Environmental Aspects, Applied Science Publishers, London, 1979.

[102] C. Fryling, High Impact Polystyrene, US Patent US3144420A, 1961.

[103] Polymerization of Styrene, Polymer Properties Database, CROW, 2015. http://polymerdatabase.com/polymer%20chemistry/Polystyrene.html (Accessed 6 January 2019).

[104] Y. Lin, X. Guo, W. Zhong, Y. Yang, Q. Du, Synthesis and characterization of polystyrene initiated using polymeric peroxide, J. Appl. Polym. Sci. 101 (1) (2006) 197—202, https://doi.org/10.1002/app.23187.

[105] H. Collins, Styrene Based Polymers (Styrenics), 2016. https://slideplayer.com/slide/9062610/ (Accessed 6 January 2019).

[106] F. Soriano, P. Acuna, G. Morales, E.D.B. Castro, Synthesis and characterization of high impact polystyrene from a heterogeneous styrene-rubber-polystyrene solution: influence of PS concentration on the phase inversion, Morphol. Impact Strength, Macromol. Symposia 325 (1) (2013) 177—183, https://doi.org/10.1002/masy.201390000.

[107] HIPS, Proprietary Process Technology, Versalis, 2018. https://www.versalis.eni.com/irj/go/km/docs/versalis/Contenuti%20Versalis/IT/Documenti/La%20nostra%20offerta/Licensing/Stirenici/ESE_Tecniche_HIPS_180214.pdf (Accessed 6 January 2019).

[108] J. Goff, T. Whelan, Dynisco Extrusion Processors Handbook, Dynisco. https://www.dynisco.com/userfiles/files/27429_Legacy_Txt.pdf. (Accessed 6 January 2019).

[109] Polystyrene — PS, AZO Materials, 2001. https://www.azom.com/article.aspx?ArticleID=798 (Accessed 7 January 2019).

[110] A. Deshpande, All you wanted to know about the amazing properties of polystyrene, ScienceStruck (2018). https://sciencestruck.com/polystyrene-properties (Accessed 7 January 2019).

[111] Polystyrene (PS) Plastic, UL Prospector. https://plastics.ulprospector.com/generics/43/polystyrene-ps. (Accessed 17 December 2018).

[112] A. Alfarraj, E.B. Nauman, Super HIPS: improved high impact polystyrene with two sources of rubber particles, Polymer 45 (25) (2004) 8435—8442, https://doi.org/10.1016/j.polymer.2004.10.005.

[113] J. Worth, Top 5 most common plastic resins for injection molding, The Rodon Group (2018). https://www.rodongroup.com/blog/top-5-most-common-plastic-resins (Accessed 22 December 2018).

[114] HIPS, Eagle Plastics. https://www.eagleplastics.co.uk/products/hips/. (Accessed 8 January 2019).

[115] Polystyrene (PS) Typical Properties Generic PS (GPPS), UL Prospector. https://plastics.ulprospector.com/generics/43/c/t/polystyrene-ps-properties-processing/sp/2. (Accessed 8 January 2019).

[116] Polystyrene (PS) Typical Properties Generic PS (HIPS), UL Prospector. https://plastics.ulprospector.com/generics/43/c/t/polystyrene-ps-properties-processing/sp/4. (Accessed 8 January 2019).

[117] R. Hemke, Why Package Your Medical Device in a Rigid Plastic? Plastic Ingenuity (2017). https://www.plasticingenuity.com/blog/rigid-plastics-for-medical-device-packaging (Accessed 7 January 2019).

[118] You Know Styrene — A resource for consumers, employees and communities, YouKnowStyrene.org. https://youknowstyrene.org/the-styrene-you-know/uses-and-benefits/. (Accessed 6 January 2019).

[119] HIPS, Plastopia. https://www.plastopialtd.com/hips/. (Accessed 7 January 2019).

[120] High Impact Polystyrene (HIPS): Techno Brief, Omnexus. https://omnexus.specialchem.com/selection-guide/high-impact-polystyrene/copy-of-applications. (Accessed 7 February 2019).

[121] Polystyrene is a Plastic, Polystyrene Packaging Council. http://www.polystyrenepackaging.co.za/educationalinformation.htm. (Accessed 7 February 2019).

[122] J. Kelly, How does polystyrene recycling work? HowStuffWorks. https://science.howstuffworks.com/environmental/green-science/polystyrene-recycling1.htm. (Accessed 7 February 2019).

[123] A. Kan, R. Demirboğa, A new technique of processing for waste-expanded polystyrene foams as aggregates, J. Mater. Process. Technol. 209 (6) (2009) 2994—3000, https://doi.org/10.1016/j.jmatprotec.2008.07.017.

[124] D.S. Achilias, E.V. Antonakou, Chemical and thermochemical recycling of polymers from waste electrical and electronic equipment, in: D.S. Achilias (Ed.), Recycling Materials Based on Environmentally Friendly Techniques, IntechOpen, London, 2014 (Chapter 3).

[125] OWA Polystyrene-HIPS 3D printing filament, 3D FilaPrint. https://shop.3dfilaprint.com/owa-ps-polystyrene-hips-black-175mm-3d-printing-filament-10282-p.asp. (Accessed 7 February 2019).

[126] High Impact Polystyrene (HIPS) Dissolvable Filament, MatterHackers. https://www.matterhackers.com/store/3d-printer-filament/hips-175mm-1kg. (Accessed 7 February 2019).

[127] PS filaments, Direct Industry. http://www.directindustry.com/industrial-manufacturer/ps-filament-226389.html. (Accessed 23 January 2019).

[128] Polystyrene — the multi-purpose 3D-printing filament, 3devo (2017). https://3devo.com/polystyrene-all-you-need-to-know/ (Accessed 8 February 2019).

[129] E. Tyson, How to 3D Print HIPS Filament — And It's Not Just a Support Material, rigid.ink. https://rigid.ink/blogs/news/how-to-3d-print-hips-filament-and-it-s-not-just-a-support-material. (Accessed 8 February 2019).

[130] HIPS, Simplify3D. https://www.simplify3d.com/support/materials-guide/hips/. (Accessed 22 January 2019).

[131] HIPS, Hestaly. https://www.hestay.nl/en/3d-print-support/3d-printer-setting-per-material/hips/. (Accessed 17 January 2019).

[132] HIPS Extrafill, Fillamentum. https://www.jacksfilament.com/datasheets/datasheet_hips_extrafill.pdf. (Accessed 17 January 2019).

[133] PS OWA, Kimya. https://www.kimya.fr/wp-content/uploads/2018/09/kimya_fiche_PS-OWA-A4-EN.pdf. (Accessed 17 January 2019).

[134] Polyvinyl Acetate, The Plastics Historical Society. http://plastiquarian.com/?page_id=14234. (Accessed 16 February 2019).

[135] S.K. Saxena, Polyvinyl Alcohol (PVA), 61st JECFA Chemical and Technical Assessment, 2004. http://www.fao.org/fileadmin/templates/agns/pdf/jecfa/cta/61/PVA.pdf (Accessed 16 February 2019).

[136] N.D. Scott, J.E. Bristol, Hydrolysis of Polymerized Vinyl Esters, US Patent US2,266,996, 1938.

[137] History of KURARAY POVAL™, Kuraray. https://www.kuraray-poval.com/aboutus/history/. (Accessed 17 February 2019).

[138] Poly(vinyl Alcohol), Merck, 2019. https://www.sigmaaldrich.com/catalog/product/aldrich/341584?lang=en&region=SI (Accessed 18 February 2019).

[139] Polyvinyl Alcohol, Encyclopædia Britannica, 2016. https://www.britannica.com/science/polyvinyl-alcohol (Accessed 20 February 2019).

[140] M.L. Hallensleben, Polyvinyl Compounds, Others in: Ullmann's Encyclopedia of Industrial Chemistry, Vol. A21, Wiley-VCH, Weinheim, 2000, pp. 743–758.

[141] C.K. Haweel, S.H. Ammar, Preparation of polyvinyl alcohol from local raw material, Iraqi, J. Chem. Petrol. Eng. 9 (1) (2008) 15–21, https://doi.org/10.31699/IJCPE.

[142] T.S. Gaaz, A.B. Sulong, M.N. Akhtar, A.A.H. Kadhum, A.B. Mohamad, A.A. Al-Amiery, Properties and applications of polyvinyl alcohol, halloysite nanotubes and their nanocomposites, Molecules 20 (2015) 22833–22847, https://doi.org/10.3390/molecules201219884.

[143] E. Rudnik, Compostable polymer materials: definitions, structures and methods of preparation, in: S. Ebnesajjad (Ed.), Handbook of Biopolymers and Biodegradable Plastics, Elsevier, Amsterdam, 2013 (Chapter 10).

[144] R. Fuss, H.-K. Mueller, Process for the Preparation of Polyvinyl Alcohol, US Patent US5914369A, 1996.

[145] Polyvinyl Alcohol, Primary Information Services, primaryinfo.com. https://www.primaryinfo.com/projects/polyvinyl-alcohol.htm. (Accessed 21 February 2019).

[146] R. Lefaux, Practical Toxicology of Plastics, CRC Press, Cleveland, 1968 (Chapter 1).

[147] Selvol™ Polyvinyl Alcohol, Sekisui Chemical, sekisui-sc.com. https://www.sekisui-sc.com/products/polyvinyl-alcohol. (Accessed 14 February 2019).

[148] J. Fromageau, E. Brusseau, D. Vray, G. Gimenez, P. Delachartre, Characterization of PVA cryogel for intravascular ultrasound elasticity imaging, IEEE Trans. Ultrason. Ferroelectrics Freq. Control 50 (10) (2003) 1318–1324, https://doi.org/10.1109/TUFFC.2003.1244748.

[149] Understanding PVA 3D Printing Filament, Center for BioMolecular Modeling, Milwaukee School of Engineering. http://cbm.msoe.edu/teacherWorkshops/printResources/documents/usingWaterPVA.pdf. (Accessed 18 February 2019).

[150] Polyvinyl Alcohol Fibers (Vinylon Fibers), Polymer Properties Database, CROW, 2017. http://polymerdatabase.com/Fibers/PVA.html (Accessed 18 February 2019).

[151] PVA Film, Joyforce Chemical Industrial. http://joyforce-chem.com/Pro_PVA_Film.html. (Accessed 14 February 2019).

[152] Vinyl Alcohol (VOH) Typical Properties Generic PVOH, UL Prospector. https://plastics.ulprospector.com/generics/59/c/t/vinyl-alcohol-voh-properties-processing/sp/2. (Accessed 14 February 2019).

[153] MOWIFLEX™, Kuraray, 2015. https://www.kuraray-poval.com/fileadmin/user_upload/KURARAY_POVAL/technical_information/brochures/mowiflex/mowiflex_for_food_casings_08072015_web.pdf (Accessed 19 February 2019).

[154] Vinyl Alcohol Polymers Are Moldable and Extrudable, Plastics Technology, 2009. https://www.ptonline.com/products/vinyl-alcohol-polymers-are-moldable-and-extrudable (Accessed 13 February 2019).

[155] Mowiflex for blown films, Kuraray. https://www.kuraray.eu/fileadmin/Downloads/Mowiflex/technical_data_sheets/TDS_Mowiflex_for_blown_films.pdf. (Accessed 13 February 2019).

[156] Ethanol, PubChem. https://pubchem.ncbi.nlm.nih.gov/compound/Ethanol#section=Top. (Accessed 13 February 2019).

[157] N. Limpan, T. Prodpran, S. Benjakul, S. Prasarpran, Influences of degree of hydrolysis and molecular weight of poly (vinyl alcohol) (PVA) on properties of fish myofibrillar protein/PVA blend films, Food Hydrocoll. 29 (1) (2012) 226–233, https://doi.org/10.1016/j.foodhyd.2012.03.007.

[158] N.H. Choulis, Miscellaneous drugs, materials, medical devices, and techniques, Side Eff. Drugs Annu. 33 (2011) 1009–1029, https://doi.org/10.1016/B978-0-444-53741-6.00049-0.

[159] Polyvinyl alcohol (PVA) Films Market Size, Share & Trends Analysis Report by Application (Detergent Backaging, Agrochemical Packaging, Laundry Bags, Embroidery), and Segment Forecasts, 2019 – 2025, Grand View Research, 2019. https://www.grandviewresearch.com/industry-analysis/polyvinyl-alcohol-films-industry (Accessed 18 February 2019).

[160] K. Qiu, A.N. Netravali, A composting study of membrane-like polyvinyl alcohol based resins and nanocomposites, J. Polym. Environ. 21 (2013) 658–674, https://doi.org/10.1007/s10924-013-0584-0.

[161] Ultimaker PVA, Ultimaker. https://ultimaker.com/en/products/materials/pva. (Accessed 18 February 2019).

[162] L. Gregurić, PVA Filament – Explained and Compared, All3DP.com. https://all3dp.com/2/pva-filament-explained-and-compared/. (Accessed 18 February 2019).

[163] PVA Filament 3D-printer Settings, Hestay. https://www.hestay.nl/en/3d-print-support/3d-printer-setting-per-material/pva/. (Accessed 18 February 2019).

[164] PVA, Simplify3D. https://www.simplify3d.com/support/materials-guide/pva/. (Accessed 18 February 2019).

[165] PVA Filament - The Easy Soluble Support Material, rigid.ink. https://rigid.ink/blogs/news/pva-the-easy-dissolvable-support-material. (Accessed 18 February 2019).

[166] Technical data sheet PVA, Ultimaker. http://3dneworld.com/wp-content/uploads/2017/08/PVA.pdf. (Accessed 18 February 2019).

[167] Acrylonitrile Butadiene Styrene (ABS) and its Features, Omnexus. https://omnexus.specialchem.com/selection-guide/acrylonitrile-butadiene-styrene-abs-plastic. (Accessed 24 January 2019).

[168] Acrylonitrile Butadiene Styrene (ABS) and Other Specialist Styrenics, British Plastic Federation. http://www.bpf.co.uk/plastipedia/polymers/ABS_and_Other_Specialist_Styrenics.aspx. (Accessed 24 January 2019).

[169] Acrylonitrile Styrene Acrylate (ASA) Plastic, UL Prospector. https://plastics.ulprospector.com/generics/8/acrylonitrile-styrene-acrylate-asa. (Accessed 24 January 2019).

[170] 2-Propenenitrile, polymer with 1,3-butadiene and ethenylbenzene, PubChem. https://pubchem.ncbi.nlm.nih.gov/compound/buta-1_3-diene_prop-2-enenitrile_styrene#section=Computed-Properties. (Accessed 24 January 2019).

[171] G. Wypych, Handbook of Polymers, second ed., ChemTec Publishing, Toronto, 2016 (Chapter 3).

[172] Acrylonitrile/styrene/butyl acrylate terpolymer, Aldrich. https://www.sigmaaldrich.com/catalog/product/aldrich/s444715?lang=en&region=si. (Accessed 24 January 2019).

[173] Polymers: An Overview, Centre for Industry Education Collaboration University of York, 2013. http://www.essentialchemicalindustry.org/polymers/polymers-an-overview.html (Accessed 3 April 2020).

[174] P. Huang, D. Tan, Y. Luo, A case study of cleaner production in acrylonitrile butadiene styrene resin companies in China, J. Environ. Sci. Technol. 3 (3) (2010) 148–158.

[175] A. Arostegui, M. Sarrionandia, J. Aurrekoetxea, I. Urrutibeascoa, Effect of dissolution-based recycling on the degradation and the mechanical properties of acrylonitrile-butadiene-styrene copolymer, Polym. Degrad. Stabil. 91 (11) (2006) 2768–2774, https://doi.org/10.1016/j.polymdegradstab.2006.03.019.

[176] F.B. Kamelian, E. Saljoughi, P.S. Nasirabadi, S.M. Mousavi, Modifications and research potentials of acryonitrile/butadiene/styrene (ABS) membranes: a review, Polym. Compos. 39 (8) (2018) 2835–2846, https://doi.org/10.1002/pc.24276.

[177] Acrylonitrile-butadiene-styrene Copolymer, Encyclopædia Britannica, 2009. https://www.britannica.com/science/acrylonitrile-butadiene-styrene-copolymer (Accessed 24 January 2019).

[178] Purer Grade of ABS Makes for Better Parts and Processes, Plastics Technology, 2019, in: https://www.ptonline.com/articles/purer-grade-of-abs-makes-for-better-parts-and-processes (Accessed 25 January 2019).

[179] ASA, Machine Design, 2002. https://www.machinedesign.com/basics-design/asa (Accessed 25 January 2019).

[180] A.J. Yu, R.E. Gallagher, Acrylate-styrene-acrylonitrile Composition and Method of Making the Same, US patent US3944631A, 1974.

[181] G.E. McKee, A. Kistenmacher, H. Goerrissen, M. Breulmann, Synthesis, properties and applications of acrylonitrile-styrene-acrylate polymers, in: J. Scheirs, D. Priddy (Eds.), Modern Styrenic Polymers: Polystyrenes and Styrenic Copolymers, John Wiley & Sons, Wiltshire, 2003, pp. 341–362.

[182] T. Rogers, Everything you need to know about ABS plastic, Creat. Mech. (2015). https://www.creativemechanisms.com/blog/everything-you-need-to-know-about-abs-plastic (Accessed 25 January 2019).

[183] P. Nugent, Rotational molding, in: M. Kutz (Ed.), Applied Plastics Engineering Handbook: Processing and Materials, 2011, pp. 311–332.

[184] ABS Plastic Properties, Adreco Plastics, 2018. https://adrecoplastics.co.uk/abs-plastic-properties-and-application/ (Accessed 25 January 2019).

[185] Acrylonitrile Styrene Acrylate (ASA), Typical Properties Generic ASA, UL Prospector. https://plastics.ulprospector.com/generics/8/c/t/acrylonitrile-styrene-acrylate-asa-properties-processing. (Accessed 28 February 2019).

[186] ASA, Performance Plastics. http://www.performance-plastics.co.uk/product/classification/asa/. (Accessed 28 February 2019).

[187] Acrylonitrile Butadiene Styrene (ABS), Typical Properties Generic ABS, UL Prospector. https://plastics.ulprospector.com/generics/1/c/t/acrylonitrile-butadiene-styrene-abs-properties-processing. (Accessed 25 January 2019).

[188] What is ABS Material? Plastic Extrusion Technologies. https://www.plasticextrusiontech.net/resources/what-is-abs-material/. (Accessed 28 February 2019).

[189] N. Niessner, H. Gausepohl, Polystyrene and styrene copolymers—an overview, in: J. Scheirs, D. Priddy (Eds.), Modern Styrenic Polymers: Polystyrenes and Styrenic Copolymers, John Wiley & Sons, Wiltshire, 2003, pp. 25–42.

[190] Acrylonitrile Styrene Acrylate (ASA), C&J Industries. http://www.cjindustries.com/wpcontent/uploads/Acrylonitrile_Styrene_Acrylate-ABA_acrylonitrile_styrene_acrylate_properties.pdf. (Accessed 1 March 2019).

[191] M.C.O. Chang, Surface defect formation in the injection molding of acrylonitrile-styrene-acrylate polymers, Int. Polym. Process. 11 (1) (1996) 76–81, https://doi.org/10.3139/217.960076.

[192] Luran S, Acrylonitrile-styrene-acrylate copolymer (ASA and ASA + PC), BASF. http://www2.basf.us/PLASTICSWEB/displayanyfile?id=0901a5e180005b42. (Accessed 1 March 2019).

[193] Extrusion processing guide: ABS – acrylonitrile-butadiene-styrene, Plastics (2016), in: https://www.plastics.gl/extrusion-profile/processing-guide-abs-acrylonitrile-butadiene-styrene/ (Accessed 2 March 2019).

[194] ASA Acrylonitrile-Styrene-Acrilate, LG Chem. http://www.lgchem.com/global/abs/asa-acrylonitrile-styrene-acrylate/product-detail-PDBDE000. (Accessed 2 March 2019).

[195] E. Leigh, The most difficult plastics to recycle, RecycleNation (2011). https://recyclenation.com/2011/03/difficult-plastics-recycle/ (Accessed 2 March 2019).

[196] Marking of Plastics Products, Chinese Standard GB/T16288–2008, Chinese Standard Publishing House, Beijing, 2008.

[197] M.F. Ashby, Materials and the Environment, second ed., Elsevier, Amsterdam, 2013, pp. pp.459–595.

[198] ASA, Simplify3D. https://www.simplify3d.com/support/materials-guide/asa/. (Accessed 10 July 2019).

[199] A. Richter, How to succeed when 3D printing with ASA filament, MatterHackers (2017). https://www.matterhackers.com/articles/how-to-succeed-when-3d-printing-with-asa-filament (Accessed 1 March 2019).

[200] J. Flynt, UV-resistant ASA filament: properties, how to use, and best brands, 3D Insider (2018). https://3dinsider.com/asa-filament/ (Accessed 7 July 2019).

[201] E. Tyson, Want to Use ABS in Hot Sun? We Compare ABS vs ASA Filaments, rigid.Ink, 2017. https://rigid.ink/blogs/news/175845063-the-difference-between-abs-and-asa (Accessed 8 July 2019).

[202] How it Works, PrintDry. https://www.printdry.com/how-to-dry-filaments/. (Accessed 8 July 2019).

[203] ABS 3D-Printer Settings, Hestay.nl. https://www.hestay.nl/en/3d-print-support/3d-printer-setting-per-material/abs/. (Accessed 8 July 2019).

[204] ABS, Simplify3D. https://www.simplify3d.com/support/materials-guide/abs/. (Accessed 8 July 2019).

[205] A. Locker, ABS filament for 3D printing – all you need to know, All3DP (2017). https://all3dp.com/abs-3d-printer-filament-explained/ (Accessed 7 July 2019).

[206] A. Richter, How to Make ABS Juice, Glue, and Slurry, 2016. https://www.matterhackers.com/news/how-to-make-abs-juice-glue-and-slurry (Accessed 7 July 2019).

[207] Get the Most Out of Your FDM 3D Printing Materials, SYS Systems. https://www.sys-uk.com/news/top-tips-when-using-fdm-3d-printing-materials/. (Accessed 7 July 2019).

[208] ASA, A UV-Stable, Production-Grade Thermoplastic for Fortus 3D Production System, SYS Systems. https://www.sys-uk.com/materials/asa/. (Accessed 8 July 2019).

[209] Technical Data Sheet ABS, Ultimaker. http://www.farnell.com/datasheets/2310520.pdf. (Accessed 8 July 2019).

[210] Technical data sheet ABS, BCN3D. https://www.bcn3dtechnologies.com/wp-content/themes/BCN3D/woocommerce/product-templates/datasheets/TDS/TDS_BCN3D_Filaments_ABS.pdf. (Accessed 8 July 2019).

[211] Technical Data Sheet ASA, Innofil3D, (2017). https://www.innofil3d.com/wp-content/uploads/2017/05/TDS-EN-Innofil3D-ASA-170529.pdf. (Accessed 17 December 2016).

[212] ASA, 3Dcompoosites. https://pro3dcomposites.com/materials/asa/. (Accessed 8 July 2019).

[213] H. Tai, Batch foaming of amorphous poly (DL-Lactic acid) and poly (lactic acid-co-glycolic acid) with supercritical carbon dioxide: CO_2 solubility, intermolecular interaction, rheology and morphology, in: J. De Vicente (Ed.), Rheology, IntechOpen, London, 2012 (Chapter 6).

[214] H. Benninga, A History of Lactic Acid Making: A Chapter in the History of Biotechnology, Kluwer Academic Publishers, Dordrecht, 1990, pp. 1–22.

[215] R.C. Bopp, NatureWorks Ingeo™Polylactide: Past, Present and Future, in: Biopolymers & Biocomposites Workshop, Iowa State University, Minnetonka, US, April 2012, pp. 1–55.

[216] M. Jamshidian, E. Arab-Tehrany, M. Imran, M. Jacquot, S. Desobry, Poly-lactic acid: production, applications, nanocomposites, and release studies, Comprehens. Rev. Food Sci. Food Safety 9 (2010) 552–571, https://doi.org/10.1111/j.1541-4337.2010.00126.x.

[217] Polylactid Acid, Polymer Properties Database, CROW, 2015. https://polymerdatabase.com/polymers/polylacticacid.html (Accessed 11 March 2019).

[218] Resomer®R202S, Poly(D,L-lactide), Merck. https://www.sigmaaldrich.com/catalog/product/aldrich/719951?lang=en&region=SI&cm_sp=Insite-_-prodRecCold_xviews-_-prodRecCold5-4. (Accessed 11 March 2019).

[219] R. Datta, M. Henry, Lactic acid: recent advances in products, processes and technologies: a review, J. Chem. Technol. Biotechnol. 81 (7) (2006) 1119–1129, https://doi.org/10.1002/jctb.1486.

[220] R. Mehta, V. Kumar, H. Bhunia, S.N. Upadhyay, Synthesis of poly(lactic acid): a review, J. Macromol. Sci. Part C: Polym. Rev. 45 (4) (2005) 325–349, https://doi.org/10.1080/15321790500304148.

[221] D. Garlotta, A literature review of poly(lactic acid), J. Polym. Environ. 9 (2) (2001) 63–84, https://doi.org/10.1023/A:1020200822435.

[222] A.J. Lasprilla, G.A. Martinez, B.H. Lunelli, A.L. Jardini, R.M. Filho, Poly-lactic acid synthesis for application in biomedical devices - a review, Biotechnol. Adv. 30 (1) (2012) 321–328, https://doi.org/10.1016/j.biotechadv.2011.06.019.

[223] S. Farah, D.G. Anderson, R. Langer, Physical and mechanical properties of PLA, and their functions in widespread applications — a comprehensive review, Adv. Drug Deliv. Rev. 107 (2016) 367–392, https://doi.org/10.1016/j.addr.2016.06.012.

[224] T. Maharana, Y.S. Negi, B. Mohanty, Melt–solid polycondensation of lactic acid and its biodegradability, Prog. Polym. Sci. 34 (1) (2009) 99–124, https://doi.org/10.1016/j.progpolymsci.2008.10.001.

[225] S. Inkinen, M. Hakkarainen, A.-C. Albertsson, A. Södergård, From lactic acid to poly(lactic acid) (PLA): characterization and analysis of PLA and its precursors, Biomacromolecules 12 (3) (2011) 523–532, https://doi.org/10.1021/bm101302t.

[226] L. Xiao, B. Wang, G. Yang, M. Gauthier, Poly(Lactic acid)-based biomaterials: synthesis, modification and applications, in: D.N. Ghist (Ed.), Biomedical Science, Engineering and Technology, IntechOpen, London, 2012, pp. 247–282.

[227] J. Lunt, Large-scale production, properties and commercial applications of polylactic acid polymers, Polym. Degrad. Stabil. 59 (1–3) (1998) 145–152, https://doi.org/10.1016/S0141-3910(97)00148-1.

[228] Polylactic Acid Properties, Production, Price, Market and Uses, Plastics Insight, 2019. https://www.plasticsinsight.com/resin-intelligence/resin-prices/polylactic-acid/ (Accessed 11 March 2019).

[229] Polylactid Acid Films, Polymer Properties Database, CROW, 2019. http://polymerdatabase.com/Films/PLA%20Films.html (Accessed 11 March 2019).

[230] The PLA, Futerro. http://www.futerro.com/products_pla.html. (Accessed 10 March 2019).

[231] Polylactic Acid (PLA) Typical Properties, UL Prospector. https://plastics.ulprospector.com/generics/34/c/t/polylactic-acid-pla-properties-processing. (Accessed 10 March 2019).

[232] Overview of materials for Polylactic Acid (PLA) Biopolymer, MatWeb. http://www.matweb.com/search/DataSheet.aspx?MatGUID=ab96a4c0655c4018a8785ac4031b9278. (Accessed 11 March 2019).

[233] J. Flynt, Polylactic acid (PLA): the environment-friendly plastic, 3D Insider (2017). https://3dinsider.com/what-is-pla/ (Accessed 10 March 2019).

[234] R.M. Johnson, L.Y. Mwaikambo, N. Tucker, Biopolymers, Rapra Rev. Rep. 14 (3) (2003) 1–26.

[235] Ingeo™ Biopolymer 2003D Technical Data Sheet, NatureWorks. https://www.natureworksllc.com/~/media/Files/NatureWorks/Technical-Documents/Technical-Data-Sheets/TechnicalDataSheet_2003D_FFP-FSW_pdf.pdf?la=en. (Accessed 9 March 2019).

[236] Processing PLA, Corbion. https://www.total-corbion.com/products/processing-pla/. (Accessed 9 March 2019).

[237] S. Suzuki, Y. Ikada, Medical applications, in: R.A. Auras, L.-T. Lim, E.M.S.E.M. Selke, H. Tsuji (Eds.), Poly(Lactic Acid): Synthesis, Structures, Properties, Processing, and Applications, 2010, pp. 443–456.

[238] P. Pan, Z. Liang, B. Zhu, T. Dong, Y. Inoue, Roles of physical aging on crystallization kinetics and induction period of poly(l-lactide), Macromolecules 41 (21) (2008) 8011–8019, https://doi.org/10.1021/ma801436f.

[239] D.E. Henton, P. Gruber, J. Lunt, J. Randall, Polylactic acid technology, in: A.K. Mohanty, M. Misra, L.T. Drzal (Eds.), Natural Fibers, Biopolymers, and Biocomposites, CRC Press, Boca Raton FL, 2005, pp. 527–577.

[240] F. Byrne, P.G. Ward, D. Hughes, J. Cullen, D.P. Dowling, Comparative Study of the Processing Conditions Required for PLA and PET Polymers, University College Dublin, Dublin, 2008.

[241] I. Pillin, N. Montrelay, A. Bourmaud, Y. Grohens, Effect of thermos-mechanical cycles on the physico-chemical properties of poly(lactic acid), Polym. Degrad. Stabil. 93 (2) (2008) 321–328, https://doi.org/10.1016/j.polymdegradstab.2007.12.005.

[242] E. Tyson, PLA 3D Printing Filament - Everything You Need to Know, rigid.Ink, 2019. https://rigid.ink/blogs/news/3d-printing-basics-how-to-get-the-best-results-with-pla-filament (Accessed 12 March 2019).

[243] Technical Data Sheet Advanced PLA, Fargo 3D Printing. https://www.fargo3dprinting.com/wp-content/uploads/2016/08/TDS-3DFuel-AdvancedPLA.pdf. (Accessed 12 March 2019).

[244] Overview of PLA - technical data, BASF. https://www.innofil3d.com/material-data/pla-technical-data/. (Accessed 12 March 2019).

[245] PLA Filament 3D-Printer Settings, Hestay.nl. https://www.hestay.nl/en/3d-print-support/3d-printer-setting-per-material/pla/. (Accessed 17 July 2019).

[246] Ingeo Biopolymer 3D850 Technical Data Sheet, NatureWorks. https://www.natureworksllc.com/~/media/Files/NatureWorks/Technical-Documents/Technical-Data-Sheets/TechnicalDataSheet_3D850_monofilament_pdf.pdf?la=en. (Accessed 16 July 2019).

[247] PLA, Simplify3D. https://www.simplify3d.com/support/materials-guide/pla/. (Accessed 17 July 2019).

[248] How to printing well with PLA Filament?, ECO. https://www.ecoreprap.com/printing-well-pla-filament/. (Accessed 16 July 2019).

[249] Best PLA 3D Printing Filaments of 2019, 3D Insider. https://3dinsider.com/pla-3d-printing-filaments/. (Accessed 16 July 2019).

[250] T. Rogers, Everything you need to know about polylactic acid (PLA), Creat. Mech. (2015). https://www.creativemechanisms.com/blog/learn-about-polylactic-acid-pla-prototypes (Accessed 17 July 2019).

[251] 3D Printing Filament Guide 2017: ABS vs PLA vs many materials, FilamentGuide.net. http://filamentguide.net/. (Accessed 17 July 2019).

[252] K. Giang, PLA vs. ABS: What's the difference?, 3D Hubs. https://www.3dhubs.com/knowledge-base/pla-vs-abs-whats-difference#part-accuracy. (Accessed 17 July 2019).

[253] How to Succeed when Printing in PLA, MatterHackers, 2013. https://www.matterhackers.com/articles/how-to-succeed-when-printing-in-pla (Accessed 16 July 2019).

[254] Technical Data Sheet PLA, Ultimaker, 2018. https://ultimaker.com/download/74599/UM180821%20TDS%20PLA%20RB%20V10.pdf (Accessed 17 July 2019).

[255] Technical Data Sheet PLA, BCN3D. https://www.bcn3dtechnologies.com/wp-content/themes/BCN3D/woocommerce/product-templates/datasheets/TDS/TDS_BCN3D_Filaments_PLA.pdf. (Accessed 17 July 2019).

[256] Nylons (Polyamide), British Plastic Federation. http://www.bpf.co.uk/plastipedia/polymers/polyamides.aspx. (Accessed 15 February 2019).

[257] Nylon, Encyclopædia Britannica. https://www.britannica.com/science/nylon. (Accessed 13 January 2019).

[258] Nylons, Polymer Science Learning Center. https://pslc.ws/macrog/nylon.htm. (Accessed 19 January 2019).

[259] E. Kuram, Z.M. Sahin, Polyamide 4,6, in: P.M. Visakh, A.O. Semkin (Eds.), High Performance Polymers and Their Nanocomposites, Wiley, Hoboken NJ, 2018 (Chapter 3).

[260] Nylon 6-6-Poly(hexamethylene adipamide), Polymer Properties Database, CROW. https://polymerdatabase.com/polymers/nylon66.html. (Accessed 19 January 2019).

[261] Nylon 6-Poly(caprolactam), Polymer Properties Database, CROW. https://polymerdatabase.com/polymers/nylon6.html. (Accessed 19 January 2019).

[262] Nylon 12-Poly(ω-dodecanamide), Polymer Properties Database, CROW. https://polymerdatabase.com/polymers/nylon12.html. (Accessed 19 January 2019).

[263] Nylon 46, Wikipedia. https://en.wikipedia.org/wiki/Nylon_46. (Accessed 19 January 2019).

[264] J.E. McIntyre, Synthetic Fibres: Nylon, Polyester, Acrylic, Polyolefin, first ed., Woodhead Publishing, Cambridge, 2005 (Chapter 1).

[265] D. Denby, C. Otter, K. Stephenson, Chemical Storylines AS, third ed., Heinemann Educational Publishers, Oxford, 2008, pp. 94−106.

[266] J.M.G. Cowie, V. Arrighi, Polymers: Chemistry and Physics of Modern Materials, third ed., CRC Press, Boca Raton FL, 2007 (Chapter 1).

[267] R.J. Palmer, Polyamides, plastics, in: H.F. Mark (Ed.), Encyclopedia of Polymer Science and Technology, forth ed. vol. 3, John Wiley & Sons, Hoboken NJ, 2001, pp. 618−644.

[268] Polymerization of Nylon-6, the National Programme on Technology Enhanced Learning, 2013. https://nptel.ac.in/courses/116102010/3 (Accessed 15 May 2017).

[269] S. Penczek, P. Kubisa, K. Matyjaszewski, Cationic ring-opening polymerization, in: Advances in Polymer Science 68/69, Springer-Verlag, Berlin Heidelberg, 1985, pp. 201−208.

[270] Synthesis of Modified Polyamides (Nylon 6), the National Programme on Technology Enhanced Learning, 2013. https://nptel.ac.in/courses/116102010/37 (Accessed 17 May 2017).

[271] Nylon, Simplify3D. https://www.simplify3d.com/support/materials-guide/nylon/. (Accessed 18 March 2019).

[272] Polyamide 66 (PA 66), Polyamide LLC company. http://anid.ru/en/poliamid/66. (Accessed 17 March 2019).

[273] M. Paloheimo, PA6/PA66-properties, Experiences and Useful Links, plasticprop.Com, 2015. https://www.plasticprop.com/articles/pa6pa66-properties-experiences-and-useful-links (Accessed 18 March 2019).

[274] What Is Polyamide (Nylon)?, Omnexus, 2018. https://omnexus.specialchem.com/selection-guide/polyamide-pa-nylon# (Accessed 17 March 2019).

[275] Nylon PA6, Pentagon Plastics. https://www.pentagonplastics.co.uk/wp-content/uploads/2015/04/Nylon-PA6.pdf. (Accessed 18 March 2019).

[276] Everything You Need to Know about Nylon (PA), Creative Mechanisms, 2016. https://www.creativemechanisms.com/blog/3d-printing-injection-molding-cnc-nylon-plastic-pa (Accessed 16 March 2019).

[277] Polyamide (Nylon) Typical Properties Generic Nylon 6, UL Prospector. https://plastics.ulprospector.com/generics/22/c/t/polyamide-nylon-properties-processing/sp/12. (Accessed 19 February 2019).

[278] Polyamide (Nylon) Typical Properties Generic Nylon 66, UL Prospector. https://plastics.ulprospector.com/generics/22/c/t/polyamide-nylon-properties-processing/sp/35. (Accessed 19 February 2019).

[279] Polyamide (Nylon) Typical Properties Generic Nylon 12, UL Prospector. https://plastics.ulprospector.com/generics/22/c/t/polyamide-nylon-properties-processing/sp/4. (Accessed 19 February 2019).

[280] Overview of materials for Nylon 12, MatWeb. http://www.matweb.com/search/DataSheet.aspx?MatGUID=0e37a459c4eb452faa9d92659f9a0ccc. (Accessed 19 February 2019).

[281] Polyamide (Nylon) Typical Properties Generic Nylon 46, UL Prospector. https://plastics.ulprospector.com/generics/22/c/t/polyamide-nylon-properties-processing/sp/9. (Accessed 19 February 2019).

[282] Overview of materials for Nylon 46, Unreinforced, MatWeb. http://www.matweb.com/search/DataSheet.aspx?MatGUID=40166ddd5f96427390986e714d58a9fb. (Accessed 19 February 2019).

[283] Top 3 Commercial Uses for Nylon, Craftech Industries. http://www.craftechind.com/top-3-commercial-uses-for-nylon/. (Accessed 17 March 2019).

[284] Polyamide 6 (PA6) NH (CH$_2$)$_5$CO Recycling, AZO Materials, 2012. https://www.azom.com/article.aspx?ArticleID=7937 (Accessed 23 June 2019).

[285] Polyamide Recycling, Greener Industry. http://www.greener-industry.org.uk/pages/nylon/8nylonPM3.htm. (Accessed 23 June 2019).

[286] P. Mägi, A. Krumme, M. Pohlak, Recycling of PA-12 in additive manufacturing and the improvement of its mechanical properties, Key Eng. Mater. 674 (2016) 9–14, https://doi.org/10.4028/www.scientific.net/KEM.674.9.

[287] B. O'Neal, Recycling multi jet fusion PA 12 powder into filament, 3DPrint.com (2019). https://3dprint.com/239797/recycling-multi-jet-fusion-pa-12-powder-into-filament/ (Accessed 23 June 2019).

[288] E. Tyson, Why 3D print with Nylon Filament? rigid.ink, 2016. https://rigid.ink/blogs/news/3d-printing-nylon-filament-heres-why-and-how-you-should-use-it (Accessed 23 June 2019).

[289] A. Chavan, 2019 nylon 3D printer guide – all about 3D printing nylon, All3DP.com (2019). https://all3dp.com/2/nylon-3d-printing-how-to-get-nylon-3d-printed/ (Accessed 17 June 2019).

[290] Filament Properties Table, Simplify3D. https://www.simplify3d.com/support/materials-guide/properties-table/. (Accessed 14 February 2019).

[291] FDM Nylon 6, Stratasys. https://www.stratasys.com/materials/search/fdm-nylon-6. (Accessed 14 February 2019).

[292] FDM Nylon 12, Stratasys. https://www.stratasys.com/materials/search/fdm-nylon-12. (Accessed 14 February 2019).

[293] Technical data Sheet Ultrafuse PA, BASF. https://www.innofil3d.com/wp-content/uploads/2019/01/Ultrafuse_PA_TDS_EN_v2.0.pdf. (Accessed 14 February 2019).

[294] J.M. Mendivil-Escalante, J.M. Gómez-Soberón, J.L. Almaral-Sánchez, R. Corral-Higuera, S.P. Arredondo-Rea, A. Castro-Beltrán, F.G. Cabrera-Covarrubias, Synthesis and characterization of PET polymer resin for your applicationin concrete, Int. J. Struct. Anal. Des. 2 (1) (2015) 105–109.

[295] Polyethylene terephthalate (PET), Plastics Historical Society. http://plastiquarian.com/?page_id=14269. (Accessed 17 December 2018).

[296] About PET, PET Resin Association. http://www.petresin.org/aboutpet.asp. (Accessed 17 December 2018).

[297] C. Geddes, Which injection grade of PBT are you looking for?, Hardie Polym. https://www.hardiepolymers.com/polymers/pbt/. (Accessed 19 December 2018).

[298] H. Sattler, M. Schweizer, Fibers, 5. Polyester fibers, in: Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2011, pp. 1–34.

[299] Substance search, Common Chemistry, ACS. http://www.commonchemistry.org/. (Accessed 27 December 2018).

[300] Poly(ethylene terephthalate), PolymerProcessing.com. http://www.polymerprocessing.com/polymers/PET.html. (Accessed 27 December 2018).

[301] Poly(butylene terephthalate), PolymerProcessing.com. http://www.polymerprocessing.com/polymers/PBT.html. (Accessed 27 December 2018).

[302] Poly(trimethylene Terephthalate), Polymer Properties Database, CROW, 2016. http://polymerdatabase.com/polymers/polytrimethyleneterephthalate.html (Accessed 27 December 2018).

[303] PETG Filament for your 3D printer, Filaments.Directory. https://www.filaments.directory/en/plastics/petg. (Accessed 16 July 2019).

[304] Polyesters, Centre for Industry Education Collaboration University of York, 2016. http://www.essentialchemicalindustry.org/polymers/polyesters.html (Accessed 28 December 2018).

[305] USEPA, Chapter 6: organic chemical process industry, in: fifth ed., in: USEPA (Ed.), AP 42, vol. I, US Environmental Protection Agency, 1991, pp. 6.6.2-1–6.6.2.13.

[306] PET – Manufacturing process of polyethylene Terephtalate, Guichon Valves. http://guichon-valves.com/faqs/pet-manufacturing-process-of-polyethylene-terephtalate-pet/. (Accessed 28 December 2018).

[307] T. Heitz, M. Klatt, R. Neuhaus, Method for the Continuous Production of Polybutyleneterephthalate from Terephthalic Acid and Butanediol, US Patent US6812321, 2004.

[308] C.H. Chan, C. Sarathchandran, T. Sabu, Poly(trimethylene Terephthalate) – the New Generation of Engineering Thermoplastic Polyester, IntechOpen, London, 2012 (Chapter 2).

[309] G. Kannan, S.E. Grieshaber, W. Zhao, Thermoplastic polyesters, in: O. Olabisi, K. Adewale (Eds.), Handbook of Thermoplastics, second ed., CRC Press, Boca Raton FL, 2016, pp. 319–330.

[310] Polyethylene terephthalate polyester (PET, PETP) - properties and applications - supplier data by goodfellow, AZO Mater. (2003). https://www.azom.com/article.aspx?ArticleID=2047 (Accessed 28 December 2018).

[311] Polyethylene Terephthalate, Encyclopædia Britannica, 2018. https://www.britannica.com/science/polyethylene-terephthalate (Accessed 27 December 2018).

[312] Polyethylene Terephthalate (PET): A Comprehensive Review, Omnexus. https://omnexus.specialchem.com/selection-guide/polyethylene-terephthalate-pet-plastic. (Accessed 27 December 2018).

[313] L. Ciera, L. Beladjal, X. Almeras, T. Gheysens, L. van Landuyt, J. Mertens, V. Nierstrasz, L. van Langenhove, Morphological and material properties of polyethyleneterephthalate (PET) fibres with spores incorporated, Fibres Text. East. Eur. 22 (4) (2014) 29–36.

[314] Complete Guide on Polybutylene Terephthalate (PBT), Omnexus. https://omnexus.specialchem.com/selection-guide/polybutylene-terephthalate-pbt-plastic. (Accessed 29 December 2018).

[315] T. Johnson, The many uses of PBT plastics, ThoughtCo (2019). https://www.thoughtco.com/what-are-pbt-plastics-820360 (Accessed 29 December 2019).

[316] Polytrimethylene terephthalate (PTT), RTP Company. https://www.rtpcompany.com/products/product-guide/polytrimethylene-terephthalate-ptt/. (Accessed 29 December 2019).

[317] F. Liu, M. Yao, M.T. Run, Synthesis and Characterizations of Poly(trimethylene terephthalate)-b-poly(tetramethylene glycol) Copolymers, Int. J. Polym. Sci. 2013 (2013) ID156289, https://doi.org/10.1155/2013/156289.

[318] PTT, Swicofil. https://www.swicofil.com/commerce/products/ptt/179/introduction. (Accessed 29 December 2019).

[319] PETG materials, Moldflow. http://www.imtechdesign.com/advice_materials_petg.php. (Accessed 29 December 2019).

[320] Polyethylene Terephthalate Glycol Market Analysis, Future Market Insights. https://www.futuremarketinsights.com/reports/polyethylene-terephthalate-glycol-market. (Accessed 28 December 2019).

[321] R. Helmke, PETG for crystal clear, Impact-Resist. Packag., Plastic Ingenuity (2016). https://www.plasticingenuity.com/blog/common-applications-for-petg (Accessed 2 February 2019).

[322] Polyester Typical Properties Generic PET, UL Prospector. https://plastics.ulprospector.com/generics/37/c/t/polyester-properties-processing/sp/16. (Accessed 17 December 2018).

[323] Overview of materials for Polyethylene Terephthalate (PET), Unreinforced, MatWeb. http://www.matweb.com/search/DataSheet.aspx?MatGUID=a696bdcdff6f41dd98f8eec3599eaa20. (Accessed 17 December 2018).

[324] Polyester Typical Properties Generic PBT, UL Prospector. https://plastics.ulprospector.com/generics/37/c/t/polyester-properties-processing. (Accessed 17 December 2018).

[325] Overview of materials for Polytrimethylene Terephthalate (PTT), MatWeb. http://www.matweb.com/search/DataSheet.aspx?MatGUID=6c56aadc6030410d895e7b8db0eb5b0f. (Accessed 17 December 2018).

[326] Polyester Typical Properties Generic PETG, UL Prospector. https://plastics.ulprospector.com/generics/37/c/t/polyester-properties-processing/sp/19. (Accessed 17 December 2018).

[327] Overview of materials for PETG Copolyester, MatWeb. http://www.matweb.com/search/DataSheet.aspx?MatGUID=4de1c85bb946406a86c52b688e3810d0. (Accessed 17 December 2018).

[328] Ultradur (PBT) Product Brochure BASF. https://products.basf.com/documents/pim;view/en/8799073544661.pdf#page=34. (Accessed 19 January 2019).

[329] PETG Copolyester 6763. Do's and Don'ts for Extruding Film, Eastman, 2012. https://www.eastman.com/Literature_Center/D/DDS1.pdf (Accessed 19 January 2019).

[330] An Introduction to PET, PET Resin Association. http://www.petresin.org/news_introtopet.asp. (Accessed 17 January 2019).

[331] PTT Compound Cost Effective Replacement Material, RTP Company. https://www.rtpcompany.com/fairing-brackets/. (Accessed 17 January 2019).

[332] R. Leblanc, Recycling Polyethylene Terephthalate, the Balance Small Business, 2019. https://www.thebalancesmb.com/recycling-polyethylene-terephthalate-pet-2877869 (Accessed 17 March 2019).

[333] L. Bartolome, B.G. Cho, D.H. Kim, M. Imran, W.A. Al-Masry, Recent developments in the chemical recycling of PET, in: D. Achilias (Ed.), Material Recycling - Trends and Perspectives, IntechOpen, London, 2012 (Chapter 2).

[334] Sink/Float Separation Tank — Plastic Recycling Machine, ASG Recycling. http://www.plasticrecyclingmachine.net/sink-float-separation-tank/. (Accessed 17 March 2019).

[335] C. Staub, PETG excluded from No. 1 resin code in California, Resour. Recycl. (2017). https://resource-recycling.com/plastics/contact/ (Accessed 18 March 2019).

[336] PET Filament: Waterproof and Food-Safe Material Plastic for 3D Printing, AllThat3D. https://www.allthat3d.com/pet-filament/. (Accessed 11 December 2019).

[337] 3D PET filament, Verbatim. https://docs.rs-online.com/450b/0900766b815ed6cf.pdf. (Accessed 15 January 2019).

[338] PETG, Simplify3D. https://www.simplify3d.com/support/materials-guide/petg/. (Accessed 11 January 2019).

[339] PBT, ZCory.com. http://www.zcory.com/prodotto/pbt/. (Accessed 11 January 2019).

[340] C.C. Ibeh, Thermoplastic Materials: Properties, Manufacturing Methods, and Applications, CRC Press, Boca Raton FL, 2011 (Chapter 15).

[341] B. Stephens, P. Azimi, Z. El Orch, T. Ramos, Ultrafine particle emissions from desktop 3D printers, Atmos. Environ. 79 (2013) 334—339, https://doi.org/10.1016/j.atmosenv.2013.06.050.

[342] MadeSolid Green PET+ Filament, MatterHackers. https://www.matterhackers.com/store/l/madesolid-green-pet-filament-300mm-1lb/sk/MXWA9TYQ. (Accessed 15 January 2019).

[343] P. Smith, PETG filament for 3D printing pros and cons, 3D Print Manual (2018). https://3dprintmanual.com/petg-filament/ (Accessed 15 January 2019).

[344] PETG Technical Data Sheet, rigid.ink. https://cdn.shopify.com/s/files/1/0714/6487/files/rigid.ink_PETG.pdf. (Accessed 17 January 2019).

[345] D. Kyriacos, Polycarbonates, in: M. Gilbert (Ed.), Brydson's Plastics Materials, eight ed., Elsevier, Amsterdam, 2017 (Chapter 17).

[346] H. Caliendo, History of BPA, Packaging Digest, 2012. https://www.packagingdigest.com/food-safety/history-bpa (Accessed 13 March 2020).

[347] A. Riley, Basics of polymer chemistry for packaging materials, in: A. Emblem, H. Emblem (Eds.), Packaging Technology: Fundamentals, Materials and Processes, Woodhead Publishing, Cambridge, 2012 (Chapter 12).

[348] V. Serini, Polycarbonates in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2000.

[349] D.J. Darensbourg, Making plastics from carbon dioxide: Salen metal complexes as catalysts for the production of polycarbonates from epoxides and CO_2, Chem. Rev. 107 (2007) 2388—2410, https://doi.org/10.1021/cr068363q.

[350] Polycarbonates, Centre for Industry Education Collaboration University of York, 2017. http://www.essentialchemicalindustry.org/polymers/polycarbonates.html (Accessed 29 December 2018).

[351] D.C. Clagett, S.J. Shafer, Polycarbonates, in: G. Allen, J.C. Bevington (Eds.), Comprehensive Polymer Science, vol. 5, Pergamon Press, Oxford, New York, 1989, pp. 345—356.

[352] Polycarbonate PC, British Plastic Federation. http://www.bpf.co.uk/plastipedia/polymers/polycarbonate.aspx. (Accessed 29 December 2018).

[353] Polycarbonate, Emco Industrial Plastics. https://www.emcoplastics.com/polycarbonate/. (Accessed 27 December 2019).

[354] Polycarbonate, IPS. https://www.ipolymer.com/pdf/Polycarbonate.pdf. (Accessed 30 December 2018).

[355] Polycarbonate, Encyclopædia Britannica, (2009). https://www.britannica.com/science/polycarbonate. (Accessed 15 January 2019).

[356] T. Rogers, Everything you need to know about polycarbonate (PC), Creat. Mech. (2015). https://www.creativemechanisms.com/blog/everything-you-need-to-know-about-polycarbonate-pc (Accessed 15 January 2019).

[357] V.R. Sastri, Plastics in Medical Devices, William Andrew, Oxford, 2010, pp. 121—173.

[358] A Complete Guide to Polycarbonate (PC), Omnexus, 2018. https://omnexus.specialchem.com/selection-guide/polycarbonate-pc-plastic (Accessed 11 January 2019).

[359] Polycarbonate (PC) Typical Properties Generic PC, UL Prospector. https://plastics.ulprospector.com/generics/25/c/t/polycarbonate-pc-properties-processing. (Accessed 11 January 2019).

[360] What is Polycarbonate? A&C Plastics. https://www.acplasticsinc.com/informationcenter/r/what-is-polycarbonate. (Accessed 11 January 2019).

[361] Polycarbonate recycling, PolycarbonateRecycling.com. http://polycarbonaterecycling.com/polycarbonate-recycling.html. (Accessed 14 February 2019).

[362] Polycarbonate sustainability, PlasticsEurope. https://studylib.net/doc/18597069/polycarbonate-sustainability. (Accessed 14 February 2019).

[363] Polycarbonate (PC) (C15H16O2) plastic recycling, AZO Mater. (2012). https://www.azom.com/article.aspx?ArticleID=7963 (Accessed 14 February 2019).

[364] Polycarbonate, Simplify3D. https://www.simplify3d.com/support/materials-guide/polycarbonate/. (Accessed December January 2019).

[365] H. Kondo, Polycarbonate (PC) 3D Printer Filament — Explained & Compared, All3DP. https://all3dp.com/2/polycarbonate-pc-filament-explained-and-compared/. (Accessed 12 January 2019).

[366] S. Cahoon, How to Succeed when Printing with Polycarbonate Filament, 2017. https://www.matterhackers.com/articles/how-to-succeed-when-printing-with-polycarbonate-filament (Accessed 12 January 2019).

[367] The Guide to Polycarbonate 3D Printing, Airwolf 3D. https://airwolf3d.com/polycarbonate-3d-printing/. (Accessed 12 January 2019).

[368] Polycarbonate Technical Data Sheet, rigid.ink. https://cdn.shopify.com/s/files/1/0714/6487/files/rigid.ink_Polycarbonate.pdf. (Accessed 12 January 2019).

[369] PC (polycarbonate), Stratasys. https://www.stratasys.com/material-spec-sheets/mss_fdm_pc_1117a. (Accessed 12 January 2019).

[370] Thermoplastic Elastomers, British Plastic Federation. https://www.bpf.co.uk/plastipedia/polymers/thermoplastic_elastomers.aspx. (Accessed 1 February 2019).

[371] Introduction to Polyurethanes, American Chemistry Council. https://polyurethane.americanchemistry.com/Introduction-to-Polyurethanes/. (Accessed 1 February 2019).

[372] Polyurethane, How Products Are Made, vol. 6, Advameg, (2010). http://www.madehow.com/Volume-6/Polyurethane.html#ixzz5fhPIEOx4. (Accessed 1 February 2019).

[373] S. Nistala, L. Hewitt, J. Horrion, S. Mishra, Thermoplastic polyurethane (TPU) in wire and cable applications, Wire&Cable India (2012). http://www.wirecable.in/2011/11/thermoplastic-polyurethane-tpu-in-wire-and-cable-applications/ (Accessed 1 February 2019).

[374] TPU meets the manufacturing challenges of a fast-changing world, Kent Elast. Prod. https://www.kentelastomer.com/tpu-meets-manufacturing-challenges-fast-changing-world/. (Accessed 19 November 2018).

[375] C. Hepburn, Polyurethane Elastomers, second ed., Springer, Amsterdam, 1992 (Chapter 9).

[376] Introduction to Thermoplastic Polyurethane (TPU) Bridging the Gap Between Rubber and Plastic, Amco Polymers, 2017. https://www.amcopolymers.com/resources/blog/introduction-to-thermoplastic-polyurethane-tpu-bridging-the-gap-between-rubber-and-plastic (Accessed 16 May 2020).

[377] J. Datta, P. Kasprzyk, K. Błażek, M. Włoch, Synthesis, structure and properties of poly(ester-urethane)s obtained using bio-based and petrochemical 1,3-propanediol and 1,4-butanediol, J. Therm. Anal. Calorim. 130 (1) (2017) 261—276, https://doi.org/10.1007/s10973-017-6558-z.

[378] J.L. Gadley, Bulk Polymerization of TPU for Reactive Processing Using RHEO-FTIR, Doctoral Dissertation, Case Western Reserve University, 2016.

[379] S. Yamasaki, Industrial synthetic methods for rubbers. 8. Polyurethane elastomers, Int. Polym. Sci. Technol. 43 (11) (2016) 29—36, https://doi.org/10.1177/0307174X1604301107.

[380] A guide to thermoplastic polyurethanes (TPU), Huntsman. http://www.huntsman.com/polyurethanes/Media%20Library/global/files/guide_tpu.pdf. (Accessed 19 November 2018).

[381] Processing of TPU by Injection Molding, Covestro, (2016). https://s3.amazonaws.com/amcopolymers.com/v3/Covestro-TPU-Processing-by-Injection-Molding.pdf. (Accessed 20 November 2018).

[382] Thermoplastic Polyurethane Elastomers (TPU), BASF, 2016. https://products.basf.com/en/Elastollan.download.html?viewType=info (Accessed 5 September 2017).

[383] Thermoplastic Polyurethane (TPU) Typical Properties Generic TPU, Unspecified, UL Prospector. https://plastics.ulprospector.com/generics/54/c/t/thermoplastic-polyurethane-tpu-properties-processing/sp/2. (Accessed 2 February 2019).

[384] Thermoplastic Elastomer (TPE) Typical Properties Generic TPE, UL Prospector. https://plastics.ulprospector.com/generics/53/c/t/thermoplastic-elastomer-tpe-properties-processing/sp/27. (Accessed 2 February 2019).

[385] All about TPU Filament, Gizmo Dorks, 2015. https://gizmodorks.com/blog/all-about-tpu-filament-/ (Accessed 15 December 2017).

[386] A. Frick, M. Borm, N. Kaound, J. Kolodziej, J. Neudeck, Microstructure and thermomechanical properties relationship of segmented thermoplastic polyurethane (TPU), AIP Conf. Proc. 1593 (1) (2014) 520—525, https://doi.org/10.1063/1.4873835.

[387] Polyurethane (PU) and Thermoplastic Polyurethane (TPU), Tudo sobre Plásticos. http://www.tudosobreplasticos.com/en/materiais/pu.asp. (Accessed 28 November 2018).

[388] Processing of TPU by Extrusion and Special Processes, Covestro, 2016, in: https://s3.amazonaws.com/amcopolymers.com/v3/Covestro-TPU-Processing-by-Extrusion-and-Special-Processes.pdf (Accessed 15 December 2017).

[389] TPU (Thermoplastic Polyurethane Elastomer), Plastopia. https://www.plastopialtd.com/tpu/. (Accessed 16 November 2018).

[390] Complete Guide on Thermoplastic Polyurethanes (TPU), Omnexus. https://omnexus.specialchem.com/selection-guide/thermoplastic-polyurethanes-tpu. (Accessed 17 February 2019).

[391] Polyurethanes and sustainability, ISOPA. http://polyurethanes.org/en/why-choose-it/sustainability-2. (Accessed 5 February 2019).

[392] Sustainability: Polyurethane Recycling, American Chemistry Council. https://polyurethane.americanchemistry.com/Polyurethane-Recycling/. (Accessed 5 February 2019).

[393] Flexible, Simplify3D. https://www.simplify3d.com/support/materials-guide/flexible/. (Accessed 10 July 2019).

[394] Ultimaker TPU 95A, Ultimaker. https://ultimaker.com/en/products/materials/tpu-95a. (Accessed 10 July 2019).

[395] E. Grames, TPU Filament — Simply Explained & Brands Compared, 2019. https://all3dp.com/2/tpu-filament-explained-and-compared/ (Accessed 27 August 2019).

[396] J. Flynt, The Properties of Flexible TPU Filament, How to Work with it, and Best Brands, 2018. https://3dinsider.com/tpu-filament/ (Accessed 27 August 2019).

[397] TPU 1.75mm 3D Printer Filament, rigid.ink. https://rigid.ink/products/tpu-1-75mm-0-03mm-tolerance?aff=2. (Accessed 10 July 2019).

[398] H. Kondo, TPE Filament — Explained and Compared, All3DP. https://all3dp.com/2/tpe-filament-explained-and-compared/. (Accessed 10 July 2019).

[399] TPE Filament: Durable, Elastic, and Versatile 3D Printing Filament, AllThat3D. https://www.allthat3d.com/tpe-filament/. (Accessed 27 August 2019).

[400] Thermoplastic Polyurethane — Advantages and Disadvantages of Thermoplastic Polyurethane, Civil Engineers Forum. https://civilengineersforum.com/thermoplastic-polyurethane-advantages-disadvantages/. (Accessed 22 December 2018).

[401] Technical data sheet TPU 95A, Ultimaker, 2018. https://ultimaker.com/download/74976/UM180821%20TDS%20TPU%2095A%20RB%20V11.pdf (Accessed 5 February 2019).

[402] Technical Data Sheet: 3DXFLEX™TPE, 3DX Flex. https://www.3dxtech.com/content/Flex_PEBAX_TPE_v1.pdf. (Accessed 5 February 2019).

[403] Filaflex®Original 82A, Recreus. https://filament2print.com/gb/index.php?controller=attachment&id_attachment=3. (Accessed 5 February 2019).

[404] A. Morita, Thermoplastic polyimide (TPI), in: J.M. Margolis (Ed.), Engineering Plastics Handbook, McGraw-Hill, New York, 2006 (Chapter 10).

[405] P.M. Visakh, High performance polymer Nanocomposites and their applications: state of the art and challenges, in: P.M. Visakh, A.O. Semkin (Eds.), High Performance Polymers and Their Nanocomposites, Wiley, Hoboken NJ, 2018 (Chapter 1).

[406] Polyetherimide (PEI): a comprehensive review, Omnexus (2018). https://omnexus.specialchem.com/selection-guide/polyetherimide-pei-high-heat-plastic (Accessed 10 March 2019).

[407] Polyetherimide, Merck. https://www.sigmaaldrich.com/catalog/search?term=61128-46-9&interface=CAS%20No.&N=0+&mode=partialmax&lang=en&region=SI&focus=product. (Accessed 10 March 2019).

[408] S. Rajasekar, D. Venkatesan, Synthesis and properties of polyetherimides by nucleophilic displacement reaction, Polym. Polym. Compos. 20 (9) (2012) 845—852, https://doi.org/10.1177/096739111202000911.

[409] R.R. Gallucci, Thermoplastic polyetherimide (PEI), in: J.M. Margolis (Ed.), Engineering Plastics Handbook, McGraw-Hill, New York, 2006 (Chapter 8).

[410] G.H. Melton, E.N. Peters, R.K. Arisman, Engineering thermoplastics, in: M. Kutz (Ed.), Applied Plastics Engineering Handbook, William Andrew, Oxford, 2011 (Chapter 2).

[411] L.W. McKeen, Fatigue and Tribological Properties of Plastics and Elastomers, William Andrew, Oxford, 2010, pp. 149—173.

[412] Poly(ether)imides (PEI), Polymer Properties Database, CROW. http://polymerdatabase.com/polymer%20classes/Polyetherimide%20type.html. (Accessed 4 February 2019).

[413] Polyetherimide, Machine Design, 2002. https://www.machinedesign.com/basics-design/polyetherimide (Accessed 4 February 2019).

[414] L.W. McKeen, Fluorinated Coatings and Finishes Handbook, William Andrew, Oxford, 2006, pp. 45—58.

[415] Polyether Imide (PEI) Typical Properties Generic PEI, UL Prospector. https://plastics.ulprospector.com/generics/28/c/t/polyether-imide-pei-properties-processing. (Accessed 7 March 2019).

[416] L.W. McKeen, Permeability Properties of Plastics and Elastomers, third ed., William Andrew, Oxford, 2012, pp. 107—120.

[417] PEI materials, Imtech Design. http://www.imtechdesign.com/advice_materials_pei.php. (Accessed 7 March 2019).

[418] ULTEM®PEI Resin Product Guide, GE Plastics. https://www.emcoplastics.com/assets/pdf/ultem/ULTEM%20Product%20Brochure%20GE.pdf. (Accessed 16 February 2019).

[419] G. Beall, Designing with polyetherimide, Plast. Today (2010). https://www.plasticstoday.com/content/designing-polyetherimide/53186273914951 (Accessed 16 February 2019).

[420] Product Data Sheet & General Processing Conditions RTP 2100 Polyetherimide (PEI), RTP Company, 2005. http://web.rtpcompany.com/info/data/2100/RTP2100.htm (Accessed 16 February 2019).

[421] Polyetherimide recycling, PolyClean Technologies. https://www.polycleantech.com/polyetherimide-recycling/. (Accessed 20 July 2019).

[422] S. Bastida, J.I. Eguiazabal, J. Nazabal, Structure and physical properties of reprocessed poly(ether imide), J. Appl. Polym. Sci. 63 (12) (1997) 1601—1607, https://doi.org/10.1002/(SICI)1097-4628(19970321)63:12<1601::AID-APP11>3.0.CO;2—2.

[423] PEI (ULTEM 1010), Filament2print. https://filament2print.com/gb/advanced/892-pei-ultem-1010.html. (Accessed 1 August 2019).

[424] Marco, PEI — Extruding the High-Performance Polymer, 3devo, 2017. https://3devo.com/blog/pei-extruding-high-performance-polymer/ (Accessed 11 March 2019).

[425] ThermaX™ PEI 3D Filament, Made using ULTEM™ 9085 PEI, 3DXTech. https://www.3dxtech.com/thermax-pei-3d-filament-made-using-ultem-9085/. (Accessed 16 March 2019).

[426] Technical Data Sheet, PEI Filament Ultem 1010, 3d4makers.com. https://www.multi-3dprint.nl/images/3d4makers/TDS_PEI_ULTEM_1010.pdf. (Accessed 1 August 2019).

[427] M. Molitch-Hou, 3D printing filaments: what's the deal with ULTEM and PEEK? Eng.com (2017). https://www.engineering.com/3DPrinting/3DPrintingArticles/ArticleID/14465/3D-Printing-Filaments-Whats-the-Deal-with-ULTEM-and-PEEK.aspx (Accessed 11 March 2019).

[428] PEI, Plastopia. https://www.plastopialtd.com/pei/. (Accessed 16 March 2019).

[429] PEEK & PEI Print Guide, Vision Miner. https://visionminer.com/pages/peek-pei-printing. (Accessed 16 July 2019).

[430] ULTEM & PEEK: The Ultimate Guide to High-Performance 3D Printing Materials, AMFG, 2018. https://amfg.ai/2018/07/09/ultem-peek-high-performance-3d-printing-materials-guide/ (Accessed 1 August 2019).

[431] PEI build surface, RepRap. https://reprap.org/wiki/PEI_build_surface. (Accessed 11 March 2019).

[432] P. Ferris, PEI Sheet for Your 3D Printer — How to Use it as a Print Surface, 2019. https://all3dp.com/2/pei-sheet-as-a-3d-printer-print-bed-sheet-a-guide/ (Accessed 11 March 2019).

[433] PEI, Nanovia. https://filament2print.com/gb/index.php?controller=attachment&id_attachment=283. (Accessed 16 July 2019).

[434] L.Q. Cortes, N. Caussé, E. Dantras, A. Lonjon, C. Lacabanne, Morphology and dynamical mechanical properties of poly ether ketone ketone (PEKK) with meta phenyl links, J. Appl. Polym. Sci. 133 (19) (2016) 1—10, https://doi.org/10.1002/app.43396.

[435] J. Norton, Poly Ether Ether Ketone (PEEK), 2019. https://www.youtube.com/watch?v=asNsbr2_xL8 (Accessed 15 August 2019).

[436] PEKK Polyether ketone ketone, Arkema. https://www.arkema.com/en/products/product-families/pekk-kepstan/. (Accessed 21 January 2019).
[437] W.H. Bonner, Aromatic Polyketones and Preparation Thereof, US patent US3065205A, 1962.
[438] E.G. Brugel, Copolyetherketones, EP patent EP0225144 A2, 1986.
[439] PEEK, Chemical Book. https://www.chemicalbook.com/ChemicalProductProperty_EN_CB9204933.htm. (Accessed 21 January 2019).
[440] Poly(ether Ketone Ketone), Polymer Properties Database, 2017. https://polymerdatabase.com/polymers/polyetherketoneketone.html (Accessed 21 January 2019).
[441] Polyetheretherketone (PEEK): A Complete Guide on High-Heat Engineering Plastic, Omnexus. https://omnexus.specialchem.com/selection-guide/polyetheretherketone-peek-thermoplastic. (Accessed 20 January 2019).
[442] G. Wu, Y. Xie, Process for Preparing a Polyether Ether Ketone, US patent US8236919B2, 2010.
[443] P.A. Staniland, Thermoplastic Aromatic Polyetherketones, EP patent, EP0184458A2, 1986.
[444] K.H. Gharda, P.D. Trivedi, V.S. Iyer, U.M. Vakil, S.C. Limaye, Melt Processible Polyether Ether Ketone Polymer, US patent US6566484B2, 2002.
[445] V. Jansons, H.C. Gors, S. Moore, R.H. Reamey, P. Becker, Preparation of Poly(arylene Ether Ketones), EP patent EP0174207A3, 1986.
[446] G.W. Rudman, G.S. O'Brien, C.A. Bertelo, Polyetherketoneketone Nonwoven Mats, US patent US9422654B2, 2012.
[447] Kepstan, Arkema. https://www.arkema.com/en/products/product-finder/range-viewer/Kepstan/. (Accessed 20 January 2019).
[448] T. Spahr, An introduction to the polyether ketone ketone(PEKK) Co-polymer, Arkema (2015). http://www.sampe.com.br/apresentacoes/2015/aeroespacial/arkema.pdf (Accessed 20 January 2019).
[449] G. Gardnier, PEEK or PEKK in future TPC aerostructures? Compos. World 4 (2018). https://www.compositesworld.com/articles/peek-or-pekk-in-future-tpc-aerostructures (Accessed 16 May 2020).
[450] M. Pacurar, M. Suciu, E.S. Bechir, A. Bechir, The benefits of polyether-ether-ketone polymers in partial edentulous patients, Mater. Plast. 53 (4) (2016) 657—660.
[451] S.J. Park, M.K. Seo, Element and processing, in: S.J. Park, M.K. Seo (Eds.), Interface Science and Composites in: Interface Science and Technology, vol. 18, Elsevier, Amsterdam, 2011, pp. 431—499.
[452] PEEK 3D printing - Tips, Examples, Advantages and More…, Tractus3D. https://tractus3d.com/3d-printing-materials/peek-3d-printing/. (Accessed 18 January 2019).
[453] Polyaryletherketone (PAEK) Typical Properties Generic PEEK, UL Prospector. https://plastics.ulprospector.com/generics/29/c/t/polyaryletherketone-paek-properties-processing/sp/4. (Accessed 2 March 2019).
[454] Overview of materials for PEKK, Unreinforced, MatWeb. http://www.matweb.com/search/DataSheet.aspx?MatGUID=b094b5b798f64ffa85bcad898bfbf57b. (Accessed 2 March 2019).
[455] Polyetherketoneketone (PEKK), Material Information, Goodfellow. http://www.goodfellow.com/A/Polyetherketoneketone-Polymer.html. (Accessed 2 March 2019).
[456] Unfilled Polyetherketoneketone (PEKK), Polymer Properties Database. http://polymerdatabase.com/Commercial%20Polymers/PEKK.html. (Accessed 2 March 2019).
[457] P. Urwyler, X. Zhao, A. Pascual, H. Schift, B. Müller, Tailoring surface nanostructures on polyaryletherketones for load-bearing implants, Eur. J. Nanomed. 6 (1) (2014) 37—46, https://doi.org/10.1515/ejnm-2014-0006.
[458] Kepstan® PEKK Resins for Extremely Demanding Applications, Arkema. https://www.extremematerials-arkema.com/en/product-families/kepstan-pekk-polymer-range/?_ga=2.129916364.1118630494.1549206568-2071993008.1549206568. (Accessed 26 January 2019).
[459] PEKK Powder Coatings, Arkema, 2011. http://www.eurometal.cz/informace-o-specialnim-povlaku-pekk (Accessed 22 September 2017).
[460] M. Sharma, H. Sharma, S. Shannigrahi, Tribology of advanced composites/biocomposites materials, in: L. Ambrosio (Ed.), Biomedical Composites, second ed., Woodhead Publishing, Cambridge, 2017, pp. 413—429.
[461] J. Walling, Replacing metals with PEEK, AZO Mater. (2013). https://www.azom.com/article.aspx?ArticleID=10147 (Accessed 22 September 2017).
[462] PEEK Injection Molding Resin, Stack Plastics. https://www.stackplastics.com/peek. (Accessed 18 January 2019).
[463] VESTAKEEP® PEEK Processing Guideline, Evonik. https://industrial.vestakeep.com/product/peek-industrial/downloads/vestakeep%20peek%20processing%2007-2016.pdf.pdf. (Accessed 26 January 2019).
[464] H. Thompson, Why PEEK is so hard to extrude, Med. Des. & Outsourcing (2018). https://www.medicaldesignandoutsourcing.com/peek-hard-extrude/ (Accessed 26 January 2019).
[465] A Comprehensive Review of the Processing Guidelines of VICTREX®PEEK™ High Performance Polymer, Victrex. https://www.emcoplastics.com/assets/pdf/peek/Processing%20Guide-PEEK.pdf. (Accessed 26 January 2019).
[466] Marco, all you need to know about PEKK, 3devo (2017). https://3devo.com/all-you-need-to-know-about-pekk/ (Accessed 18 January 2019).
[467] GAPEKK — Polyether Ketone Ketone, Performance Plastics. http://www.performance-plastics.co.uk/wp-content/uploads/GAPEKK-3300G.pdf. (Accessed 18 January 2019).
[468] M. Lauzon, Diversified Plastics, PEEK playing role in space probe, Plast. News (2012). https://www.plasticsnews.com/article/20120504/NEWS/305049956/diversified-plastics-inc-peek-playing-role-in-space-probe (Accessed 22 September 2017).
[469] PEEK (Polyaryletheretherketone), British Plastic Federation. https://www.bpf.co.uk/plastipedia/polymers/peek.aspx. (Accessed 18 January 2019).
[470] What is Polyethererketone? (PEEK), Fluorocarbon Company, 2016. http://www.fluorocarbon.co.uk/news-and-events/post/13/what-is-polyethererketone-peek (Accessed 17 December 2019).
[471] PEEK 3D printing, INTAMSYS. https://www.intamsys.com/peek-3d-printing/. (Accessed 14 July 2019).
[472] Polyetherketoneketones (PEKK), Polymer Properties Database. http://polymerdatabase.com/Polymer%20Brands/PEKK.html. (Accessed 18 January 2019).
[473] PEKK, Filament2print. https://filament2print.com/gb/advanced/899-pekk.html. (Accessed 14 July 2019).
[474] Polyether ether ketone (PEEK) recycling, AZO Mater. (2012). https://www.azom.com/article.aspx?ArticleID=7989 (Accessed 8 March 2019).

[475] Polyketone (PEEK) Plastics, Power Plastic Recycling. https://powerplasticrecycling.com/peek-plastic/. (Accessed 8 March 2019).

[476] PEEK-Thermoplastic, Minger. https://www.minger.ch/produkte/peek-kunststoff/?lang=en. (Accessed 14 July 2019).

[477] PEEK, Vision Miner, 2019. https://visionminer.com/products/peek (Accessed 14. July 2019).

[478] D. Sher, Everything about today's PEEK 3D printing market, 3dpbm (2018). https://www.3dprintingmedia.network/everything-about-peek-3d-printing/ (Accessed 8 March 2019).

[479] Focus on Materials: PEKK-A, Armor, 2018. https://www.kimya.fr/en/focus-on-materials-peek-a/ (Accessed 12 September 2019).

[480] ThermaX™ PEEK 3D Printing Filament [NATURAL], 3DXTECH. https://www.3dxtech.com/peek-3d-printing-filament/. (Accessed 12 September 2019).

[481] 3DXSTAT™ ESD-PEKK 3D Printing Filament, 3DXTECH. https://www.3dxtech.com/3dxstat-esd-pekk-3d-printing-filament/. (Accessed 12 September 2019).

[482] Best practices in 3D printing PEEK FDM filament, 3D4 Make. (2017). https://www.3d4makers.com/blogs/news/best-practices-in-3d-printing-peek-fdm-filament (Accessed 11 July 2019).

[483] V. Carlota, How to 3D Print High-Performance Materials (PAEK, PEI…)? Experts Give Their Advice!, 3Dnatives, 2019. https://www.3dnatives.com/en/high-performance-materials-190620194/ (Accessed 12 September 2019).

[484] A. Haleem, M. Javaid, Polyether ether ketone (PEEK) and its 3D printed implants applications in medical field: an overview, Clin. Epidemiol. and Glob. Health 7 (4) (2019) 571—577, https://doi.org/10.1016/j.cegh.2019.01.003.

[485] 3D Printing with PEKK - Stratasys Antero 800NA, GoEngineer, 2018. https://www.youtube.com/watch?v=iIbPGyWJnBw (Accessed 8 March 2019).

[486] Thermoplastics as a Substitute for Metal Additive Manufacturing?, Tractus3D. https://tractus3d.com/3d-printing-materials/3d-printing-thermoplastics-substitute-metal-additive-manufacturing/. (Accessed 8 March 2019).

[487] LUVOCOM 3F PEEK 9581 NT, Lehvos. https://www.luvocom.de/fileadmin/user_upload/luvomaxx/Downloads/LUVOCOM_3F_PEEK_9581_NT.pdf. (Accessed 12 September 2019).

[488] Technical Data Sheet KetaSpire® MS NT1 AM Filament, Solvay, https://catalog.ides.com/Datasheet.aspx?I=92041&FMT=PDF&U=0&CULTURE=en-US&E=386929. (Accessed 12 September 2019).

[489] Technical Data Sheet PEEK Filament, 3D4 Makers. https://www.multi-3dprint.nl/images/3d4makers/TDS_PEEK_Filament_1.pdf. (Accessed 12 September 2019).

[490] KEPSTAN by ARKEMA, PEKK vs. PEEK in FF, Arkema. https://www.extremematerials-arkema.com/en/product-families/kepstan-pekk-polymer-range/?_ga=2.26601149.1266470640.1567959074-323603349.1567959041. (Accessed 12 September 2019).

[491] Native PEKK JNM 2712N, Nanovia. https://filament2print.com/gb/index.php?controller=attachment&id_attachment=290. (Accessed 12 September 2019).

[492] Antero 800NA, Stratasys. https://www.stratasys.com/materials/search/antero-800na. (Accessed 12 September 2019).

[493] S.A. Weinberg, J. El-Hibri, Polyarylethersulfones (PAES), in: J.M. Margolis (Ed.), Engineering Plastics Handbook, McGraw-Hill, New York, 2006 (Chapter 13).

[494] R.A. Clendinning, A.G. Farnham, R.N. Johnson, The development of polysulfone and other polyarylethers, in: R.B. Seymour, G.S. Kirshenbaum (Eds.), High Performance Polymers: Their Origin and Development, Proceedings of the Symposium on the History of High Performance Polymers at the American Chemical Society, April 15—18 1986, New York, 1986, pp. 149—158.

[495] M.J. El-Hibri, S.W. Axelrad, Polyarylethersulfones, in: O. Olabisi, K. Adewale (Eds.), Handbook of Thermoplastics, CRC Press, Boca Raton FL, 2015, pp. 419—460.

[496] Polysulfone, PolymerProcessing.com. http://www.polymerprocessing.com/polymers/PSU.html. (Accessed 9 January 2019).

[497] Poly(phenylsulfone), Polymer Properties Database, 2015. http://polymerdatabase.com/polymers/polyphenylsulfone.html (Accessed 9 January 2019).

[498] M. Volkel, N. Herz, Polyarylsulfones (PSU, PESU, PPSU), Kunstoffe Int. 10 (2010) 109—111.

[499] Ultrason E, S, P (PESU, PSU, PPSU) Product Brochure, BASF, 2013. http://www8.basf.us//PLASTICSWEB/displayanyfile?id=0901a5e18039b910 (Accessed 13 January 2019).

[500] Technical Data Sheet Radel® R-5000 Polyphenylsulfone, Solvay, 2019. https://catalog.ides.com/datasheet.aspx?I=42041&FMT=PDF&E=1445 (Accessed 13 January 2019).

[501] C.A. Harper, Fundamentals of plastics and elastomers, in: C.A. Harper (Ed.), Handbook of Plastics and Elastomers, McGraw Hill, New York, 1975 (Chapter 1).

[502] Polyphenylsulfone (PPSU, PPSF), Polymer Properties Database, 2018. http://polymerdatabase.com/Polymer%20Brands/PPSU.html (Accessed 13 January 2019).

[503] Polysulfone (PSU) Typical Properties Generic PPSU, UL Prospector. https://plastics.ulprospector.com/generics/44/c/t/polysulfone-psu-properties-processing/sp/2. (Accessed 16 January 2019).

[504] Overview of materials for Polysulfone (PSU), MatWeb. http://www.matweb.com/search/DataSheet.aspx?MatGUID=83fc0624f2ea4bb4aa54293621471312. (Accessed 16 January 2019).

[505] Polysulfone (PSU) Typical Properties Generic PSU, UL Prospector. https://plastics.ulprospector.com/generics/44/c/t/polysulfone-psu-properties-processing/sp/3. (Accessed 16 January 2019).

[506] Overview of materials for Polyphenylsulfone (PPSU), MatWeb. http://www.matweb.com/search/DataSheet.aspx?MatGUID=801427233e964766bcc21712fba42302. (Accessed 16 January 2019).

[507] FDM 3D printing of PPSU PPSF polyphenylsulfone radel best practices, 3D4 Makers (2017). https://www.3d4makers.com/blogs/news/fdm-3d-printing-of-ppsu-ppsf-polyphenylsulfone-best-practices (Accessed 9 January 2019).

[508] Ultrason E, S, P (PESU, PSU, PPSU), Ultrason_brochure_en.pdf, BASF, 2016. https://products.basf.com/en/Ultrason.industry~plastics_rubber%7Cperformance_polymers.html (Accessed 13 January 2019).

[509] Processing of BASF Thermoplastics in Extrusion, BASF. https://plastics-rubber.basf.com/en/Performance-Polymers/Extrusion.html. (Accessed 13 January 2019).

[510] Thermax™ PSU 3D Printing Filament, 3DXTech. https://www.3dxtech.com/firewire-psu-3d-printing-filament/. (Accessed 16 January 2019).

[511] Polyarylsulfone (PSU/P/PPSU), PAGEV. https://www.pagev.org/psu-p-ppsu-en. (Accessed 16 January 2019).

[512] Thermax™ PPSU 3D Printing Filament, 3DXTech. https://www.3dxtech.com/thermax-ppsf-ppsu-3d-printing-filament/. (Accessed 27 January 2019).

[513] PPSU filament Technical Data Sheet, 3D4 Makers. https://www.multi-3dprint.nl/images/3d4makers/TDS_PPSU_Filament.pdf. (Accessed 28 January 2019).

[514] PPSF/PPSU, CIDEAS. http://www.buildparts.com/materials/ppsf. (Accessed 27 January 2019).

[515] S. Gottgens, W. Sanner, Polysulfones (PSU, PESU, PPSU), Kunstoffe Int. 10 (2005) 139−142.

[516] G. Breiland, Woolf-Proofing and resin choice. http://digital.bnpmedia.com/publication. (Accessed 27 January 2019).

[517] Polysulfone (PSU), C&J Industries. http://www.cjindustries.com/wp-content/uploads/Polysulfone_Resins-PSU-Thermoplastic_Molding_Materials-Polysulfone_Resin_Properties.pdf. (Accessed 28 January 2019).

[518] R. Haria, First ever Polysulfone mold for Chinook helicopter part successfully 3D printed, 3D Print. Indus. (2017). https://3dprintingindustry.com/news/first-ever-polysulfone-mold-chinook-helicopter-part-successfully-3d-printed-123142/ (Accessed 16 January 2019).

[519] Additive ManufacturingFilaments Processing Guide Specialty Polymers, Solvay. https://www.solvay.com/sites/g/files/srpend221/files/2018-11/Additive-Manufacturing-Filaments-Processing-Guide_EN-v1.1_0.pdf. (Accessed 27 January 2019).

[520] PPSF/PPSU, Javelin. https://www.javelin-tech.com/3d/stratasys-materials/ppsf-ppsu/. (Accessed 27 January 2019).

[521] TECAFIL PPSU natural − Filament, Ensinger. https://www.ensingerplastics.com/en/datasheets?term=TECAFIL%20PPSU. (Accessed 13 July 2019).

[522] TECAFIL PSU natural − Filament, Ensinger. https://www.ensingerplastics.com/en/datasheets?term=TECAFIL%20PSU. (Accessed 13 July 2019).

[523] ThermaX™ PSU 3D Printing Filament, 3DXTech. https://www.3dxtech.com/content/UN_PSU_v3.pdf. (Accessed 13 July 2019).

[524] K. Bryll, E. Piesowicz, P. Szymański, W. Ślączka, M. Pijanowski, Polymer composite manufacturing by FDM 3D printing technology, MATEC Web of Conf. 237 (2018) 02006, https://doi.org/10.1051/matecconf/201823702006.

[525] X. Wang, M. Jiang, Z. Zhou, J. Gou, D. Hui, 3D printing of polymer composites: a review and prospective, Compos. B Eng. 110 (2017) 442−458, https://doi.org/10.1016/j.compositesb.2016.11.034.

[526] L.G. Blok, M.L. Longana, H. Yu, B.K.S. Woods, An investigation into 3D printing of fibre reinforced thermoplastic composites, Addit. Manuf. 22 (2018) 176−186, https://doi.org/10.1016/j.addma.2018.04.039.

[527] B. Singh, R. Kumar, J.S. Chohan, Polymer matrix composites in 3D printing: A state of art review, Mater. Today Proc. Available from: <https://doi.org/10.1016/j.matpr.2020.04.335>.

[528] P.K. Penumakala, J. Santo, A. Thomas, A critical review on the fused deposition modeling of thermoplastic polymer composites, composites part B: Engineering 201 (2020) 108336, https://doi.org/10.1016/j.compositesb.2020.108336.

[529] A. Locker, 2019 metal 3D printer guide − all about metal 3D printing, All 3DP (2019). https://all3dp.com/1/3d-metal-3d-printer-metal-3d-printing/ (Accessed 1 September 2019).

[530] M. Stevenson, 3D printer metal filament − 2018 market overview, All 3DP (2018). https://all3dp.com/2/3d-printer-metal-filaments-2018-market-overview/ (Accessed 3 September 2019).

[531] A.K. Shrivastav, 3D printer metal filament: the basics & best brands, All 3DP (2020). https://all3dp.com/2/3d-printer-metal-filament-basics-best-brands/ (Accessed 15 August 2020).

[532] 16 Different Types of 3D Printing Materials, 3D Insider. https://3dinsider.com/3d-printing-materials/. (Accessed 1 September 2019).

[533] How to print with copperFill, ColorFabb, (2014). http://learn.colorfabb.com/print-copperfill/. (Accessed 1 September 2019).

[534] Metal filled, Simplify3D. https://www.simplify3d.com/support/materials-guide/metal-filled/. (Accessed 2 September 2019).

[535] ColorFabb bronzeFill Metal Filament - 1.75mm (0.75kg), MatterHackers. https://www.matterhackers.com/store/l/colorfabb-bronzefill-175-750g/sk/M1K5FLJH. (Accessed 2 September 2019).

[536] ColorFabb copperFill Metal Filament - 1.75mm (0.75kg), MatterHackers, https://www.matterhackers.com/store/l/colorfabb-copperfill-metal-filament-1.75mm-075-kg/sk/MRM2EVUL. (Accessed 2 Sepetember 2019).

[537] ColorFabb SteelFill Filament - 1.75mm (0.75kg), MatterHackers. https://www.matterhackers.com/store/l/colorfabb-steelfill-filament-1.75mm-0.75kg/sk/M6A2VGNM. (Accessed 2 September 2019).

[538] MetalFil - Ancient Bronze, Formfutura. https://www.formfutura.com/shop/product/metalfil-ancient-bronze-252. (Accessed 2 September 2019).

[539] MetalFil − Classic Copper, Formfutura. https://www.formfutura.com/shop/product/metalfil-classic-copper-253?category=117. (Accessed 2 September 2019).

[540] A quick guide to exotic FDM printing materials, Treatstock. https://www.treatstock.co.uk/guide/article/123-a-quick-guide-to-exotic-fdm-printing-materials. (Accessed 8 September 2019).

[541] C. Huber, C. Abert, F. Bruckner, M. Groenefeld, O. Muthsam, S. Schuschnigg, K. Sirak, R. Thanhoffer, I. Teliban, C. Vogler, R. Windl, D. Suess, 3D print of polymer bonded rare-earth magnets, and 3D magnetic field scanning with an end-user 3D printer, Appl. Phys. Lett. 109 (16) (2016) 162401, https://doi.org/10.1063/1.4964856.

[542] J. Chu, Magnetic 3-D-printed structures crawl, roll, jump, and play catch, MIT News (2018). https://news.mit.edu/2018/magnetic-3-d-printed-structures-crawl-roll-jump-play-catch-0613 (Accessed 8 September 2019).

[543] Iron-filled Metal Composite PLA. ProtoPlant. https://www.proto-pasta.com/products/magnetic-iron-pla. (Accessed 7 September 2019).

[544] J. Flynt, Magnetic filaments: properties, applications, how to use them, and best brands, 3D Insider (2018). https://3dinsider.com/magnetic-filament/ (Accessed 7 September 2019).

[545] 3D Printer Filament Types Guide of 2019, AllThat3D, 2019. https://www.allthat3d.com/3d-printer-filament/ (Accessed 1 September 2019).

[546] Magnetic Iron PLA, Vexma Technologies. https://vexmatech.com/magnetic-iron-pla.html. (Accessed 8 September 2019).

[547] J. Flynt, The curious case of conductive filaments, 3D Insider (2018). https://3dinsider.com/conductive-filament/ (Accessed 9 September 2019).

[548] S.W. Kwok, K.H.H. Goh, Z.D. Tan, S.T.M. Tan, W.W. Tjiu, J.Y. Soh, Z.J.G. Ng, Y.Z. Chan, H.K. Hui, K.E.J. Goh, Electrically conductive filament for 3D-printed circuits and sensors, Appl. Mater. Today 9 (2017) 167−175, https://doi.org/10.1016/j.apmt.2017.07.001.

[549] B.Y. Ahn, E.B. Duoss, M.J. Motala, X. Guo, S.I. Park, Y. Xiong, J. Yoon, R.G. Nuzzo, J.A. Rogers, J.A. Lewis, Omnidirectional printing of flexible, stretchable, and spanning silver microelectrodes, Science 323 (5921) (2009) 1590–1593, https://doi.org/10.1126/science.1168375.

[550] M. von Übel, 2019 3D printing materials guide – all you need to know, All3DP (2019). https://all3dp.com/1/3d-printing-materials-guide-3d-printer-material/ (Accessed 3 September 2019).

[551] Conductive PLA, Protoplant. https://www.proto-pasta.com/pages/conductive-pla#CCcoductivity. (Accessed 7 September 2019).

[552] Conductive PLA Filament, ECO. https://www.ecoreprap.com/conductive-pla-filament/#tab-id-1. (Accessed 7 September 2019).

[553] J. Flynt, Sturdy carbon fiber filament: properties, how to .se, and best brands, 3D Insider (2018). https://3dinsider.com/carbon-fiber-filament/ (Accessed 9 September 2019).

[554] Carbon Fiber Filled, Simplify3D. https://www.simplify3d.com/support/materials-guide/carbon-fiber-filled/. (Accessed 9 September 2019).

[555] C. Weiss, Understanding the role of carbon fiber in 3D printing, Markforged (2018). https://www.rdmag.com/article/2018/10/understanding-role-carbon-fiber-3d-printing (Accessed 8 September 2019).

[556] Carbon Fiber Filaments, 3DXTech. https://www.3dxtech.com/carbon-fiber/. (Accessed 8 September 2019).

[557] CarbonX™ CFR Carbon Fiber Reinforced PLA Filament, 3DXTech. https://www.3dxtech.com/carbonx-carbon-fiber-pla-3d-printing-filament-1/. (Accessed 8 September 2019).

[558] CarbonX™ CFR-ABS carbon fiber reinforced ABS 3D printing filament, Merck. https://www.sigmaaldrich.com/catalog/product/aldrich/3dxcfr003?lang=en&region=SI&cm_sp=Insite-_-prodRecCold_xviews-_-prodRecCold10-1. (Accessed 8 September 2019).

[559] CarbonX™ Carbon Fiber ABS 3D Printing Filament, 3DXTech. https://www.3dxtech.com/carbonx-carbon-fiber-abs-3d-printing-filament/. (Accessed 8 September 2019).

[560] CarbonX™ Carbon Fiber PETG 3D Printing Filament, Performance 3-d. https://www.p3-d.com/products/carbonx-carbon-fiber-petg-3d-printing-filament. (Accessed 8 September 2019).

[561] CarbonX™ Carbon Fiber Reinforced Polycarbonate (PC) Filament, 3DXTech. https://www.3dxtech.com/carbonx-carbon-fiber-pc-3d-printing-filament/. (Accessed 8 September 2019).

[562] CarbonX™ Carbon Fiber NYLON (Gen 3) 3D Printing Filament, 3DXTech. https://www.3dxtech.com/carbonx-carbon-fiber-nylon-gen-3-3d-printing-filament/. (Accessed 8 September 2019).

[563] CarbonX™ Carbon Fiber PEEK 3D Printing Filament, 3DXTech. https://www.3dxtech.com/carbonx-carbon-fiber-peek-3d-printing-filament/. (Accessed 8 September 2019).

[564] CarbonX™ Carbon Fiber PEKK (Industrial) 3D Printing Filament, 3DXTech. https://www.3dxtech.com/carbonx-carbon-fiber-pekk-industrial-3d-printing-filament/. (Accessed 8 September 2019).

[565] CarbonX™ Carbon Fiber Reinforced PEI, Performance 3-d. https://www.p3-d.com/collections/filament/products/carbonx-carbon-fiber-ultem-3d-printing-filament. (Accessed 8 September 2019).

[566] Technical data Sheet: CarbonX™ CF-PLA 3D Filament, 3DXTech. https://www.3dxtech.com/content/CF_PLA_v3.pdf. (Accessed 9 September 2019).

[567] CarbonX™ Carbon Fiber Reinforced ABS 3D Filament, 3DXTech. https://cdn.shopify.com/s/files/1/0965/1648/files/Carbon_Fiber_ABS_Filament_v2.1.pdf?8887840607194897647. (Accessed 9 September 2019).

[568] Technical data Sheet: CarbonX™ Carbon Fiber Polycarbonate 3D Filament, 3DXTech. https://www.3dxtech.com/content/CF_PC_v3.pdf. (Accessed 9 September 2019).

[569] CarbonX™ Carbon Fiber Reinforced PETG 3D Filament, 3DXTech. https://cdn.shopify.com/s/files/1/0965/1648/files/Carbon_Fiber_PETG_Filament_v2.1.pdf?10212164970777640663. (Accessed 9 September 2019).

[570] Technical Data Sheet: CarbonX™ Carbon Fiber Nylon (Gen3) 3D Printing Filament, 3DXTech. https://www.3dxtech.com/content/CF_Nylon_Gen3_v3.pdf. (Accessed 9 September 2019).

[571] Technical Data Sheet: CarbonX™ Carbon Fiber PEEK 3D Filament, 3DXTech. https://www.3dxtech.com/content/CF_PEEK_v3.pdf. (Accessed 9 September 2019).

[572] Technical Data Sheet: CarbonX™ Carbon Fiber PEKK 3D Printing Filament, 3DXTech. https://www.3dxtech.com/content/CF_PEKK_Dual_v4.pdf. (Accessed 9 September 2019).

[573] Technical Data Sheet: CarbonX™ Carbon Fiber Ultem™ PEI 3D Printing Fillament. 3DXTech. https://www.3dxtech.com/content/CF_Ultem_v3.pdf. (Accessed 9 September 2019).

[574] S.J. Liu, Injection molding in polymer matrix composites, in: E. Suresh, G. Advani, K.-T. Hsiao (Eds.), Manufacturing Techniques for Polymer Matrix Composites (PMCs), Woodhead Publishing, Cambridge, 2012, pp. 15–46.

[575] T.P. Sathishkumar, S. Satheeshkumar, J. Naveen, Glass fiber-reinforced polymer composites - a review, J. Reinforc. Plast. Compos. 33 (13) (2014) 1258–1275, https://doi.org/10.1177/0731684414530790.

[576] B. Krassenstein, 3Dom USA Unveils Glass Filled PLA 3D Printer Filament, 3DPrint.Com, 2015. https://3dprint.com/85153/3dom-usa-glass-filled-pla/ (Accessed 10 September 2019).

[577] NylonG Glass Fiber Reinforced Nylon, MatterHackers. https://www.matterhackers.com/store/c/nylong. (Accessed 10 September 2019).

[578] Fiberglass Filament, Markforged. https://markforged.com/materials/fiberglass/. (Accessed 10 September 2019).

[579] A. Crease, Fiber Reinforced 3D Printing: What You Need to Know, Markforged. https://markforged.com/learn/fiber-reinforced-3d-printing-what-you-need-to-know/. (Accessed 10 September 2019).

[580] Fiber-Reinforced Nylon: 3D Hubs Releases Kevlar, Carbon & Fiberglass Materials for Strong Yet Affordable 3D Printing, 3DPrint.com. https://3dprint.com/135398/fiber-reinforced-nylon-3d-hubs/. (Accessed 11 September 2019).

[581] AmideX™ PA6-GF30 Glass Fiber Reinforced Nylon, 3DXTech. https://www.3dxtech.com/amidex-pa6-gf30-glass-fiber-reinforced-nylon/. (Accessed 11 September 2019).

[582] Black NylonG Glass Fiber Filament - 1.75mm (0.5kg), MatterHackers. https://www.matterhackers.com/store/l/black-nylong-175-05/sk/M49RPFYR. (Accessed 11 September 2019).

[583] Technical Data Sheet PolyMide™ PA6-GF, Polymaker. https://polymaker.com/Downloads/TDS/PolyMide_%20PA6-GF_TDS_EN_V4.pdf. (Accessed 10 September 2019).

[584] T. Vialva, DuPont debuts industrial carbon and glass-reinforced 3D printing filaments at formnext, 3D Print. Indus. (2018). https://3dprintingindustry.com/news/dupont-debuts-industrial-carbon-and-glass-reinforced-3d-printing-filaments-at-formnext-144124/ (Accessed 11 September 2019).

[585] XSTRAND™ Glass Fiber Reinforced Polypropylene GF30-PP - 1.75mm, 3D Printing Network. https://filaments.ca/products/xstrand-glass-fiber-reinforced-polypropylene-gf30-pp-1-75mm. (Accessed 12 September 2019).

[586] 3DXMAX® ABS-GF10 Glass Fiber Reinforced ABS, 3DXTech. https://www.3dxtech.com/3dxmax-abs-gf10-glass-fiber-reinforced-abs/. (Accessed 12 September 2019).

[587] MAX-G™ GF-20 Glass Fiber Reinforced PETG, 3DXTech. https://www.3dxtech.com/max-g-gf-20-glass-fiber-reinforced-petg-discontinued/. (Accessed 12 September 2019).

[588] ThermaX™ PEEK-GF20 Glass Fiber Reinforced PEEK 3D Printing Filament, 3DXTech. https://www.3dxtech.com/thermax-peek-gf20-glass-fiber-reinforced-peek-3d-printing-filament/. (Accessed 13 September 2019).

[589] ThermaX™ PEI-GF10 Glass Fiber Reinforced 3D Filament, Made using ULTEM™ PEI, 3DXTech. https://www.3dxtech.com/thermax-pei-gf10-glass-fiber-reinforced-3d-filament-made-using-ultem-pei/. (Accessed 13 September 2019).

[590] PolyMide™ PA6-GF, Polymaker. https://eu.polymaker.com/product/polymide-pa6-gf/. (Accessed 14 September 2019).

[591] Material Datasheet Composites, Markforged. http://static.markforged.com/downloads/composites-data-sheet.pdf. (Accessed 14 September 2019).

[592] Technical Data Sheet: GlassX™ Glass-Fiber PETG 3D Printing Filament, 3DXTech. https://www.3dxtech.com/content/GF_PETG_v3.pdf. (Accessed 14 September 2019).

[593] PLA-HI-GF10 3D printer filament, Clariant. https://www.3d-printerstore.ch/media/content/Clariant/TDS/PLA-HI-GF10.pdf. (Accessed 14 September 2020).

[594] B. Khatri, K. Lappe, M. Habedank, T. Mueller, C. Megnin, T. Hanemann, Fused deposition modeling of ABS-barium titanate composites: a simple route towards tailored dielectric devices,, Polymers 10 (6) (2018) 666, https://doi.org/10.3390/polym10060666.

[595] S. Danforth, Fused deposition of ceramics: a new technique for the rapid fabrication of ceramic components, Mater. Technol. 10 (7–8) (1995) 144–146, https://doi.org/10.1080/10667857.1995.11752614.

[596] S. Iyer, J. McIntosh, A. Bandyopadhyay, N. Langrana, A. Safari, S. Danforth, R. Clancy, C. Gasdaska, P. Whalen, Microstructural characterization and mechanical properties of Si3N4 formed by fused deposition of ceramics, Int. J. Appl. Ceram. Technol. 5 (2) (2008) 127–137, https://doi.org/10.1111/j.1744-7402.2008.02193.x.

[597] D. Nötzel, R. Eickhoff, T. Hanemann, Fused filament fabrication of small ceramic components, Materials 11 (8) (2018) 1463, https://doi.org/10.3390/ma11081463.

[598] Z. Chen, Z. Li, J. Li, C. Liu, C. Lao, Y. Fu, C. Liu, Y. Li, P. Wang, Y. He, 3D printing of ceramics: a review, J. Eur. Ceram. Soc. 39 (4) (2019) 661–687, https://doi.org/10.1016/j.jeurceramsoc.2018.11.013.

[599] M. Molitch-Hou, Kai Parthy's Latest Experimental Filament: LAYCeramic, 3D Printing Industry, 2014. https://3dprintingindustry.com/news/3d-printing-filament-kai-parthy-24978/ (Accessed 14 September 2019).

[600] LAY-CERAMIC (Contains Clay) Hardware Requirements and Instructions How to Sinter, 2017. https://www.dropbox.com/s/3mst782b64mutzb/LAYCERAMIC-Instructions-7-2017-public.pdf?dl=0 (Accessed 15 September 2019).

[601] J. Flynt, Sandstone filament: properties, how to use them, and best brands, 3D Insider (2018). https://3dinsider.com/sandstone-filament/ (Accessed 15 September 2019).

[602] Smartfil EP (Ceramic), filament2print. https://filament2print.com/gb/wood-ceramic/762-smartfil-ep-limestone.html. (Accessed 15 September 2019).

[603] Smartfil E.P., filament2print. https://filament2print.com/gb/index.php?controller=attachment&id_attachment=63. (Accessed 15 September 2019).

[604] LayBrick Sandstone Filament - 1.75 mm - 250g, 3D Prima. https://www.3dprima.com/filaments/a-20287. (Accessed 15 September 2019).

[605] Technical Datasheet LAYWOOD-LAYBRICK-BENDLAY, German RepRap. https://www.germanreprap.com/en/materialdatasheets.aspx. (Accessed 15 September 2019).

[606] M. Theias, Wood 3D printer – all about wood 3D printing in 2019, All3DP (2019). https://all3dp.com/2/wood-3d-printer-all-you-need-to-know-about-wood-3d-printing-2/ (Accessed 16 September 2019).

[607] M. Kariž, M. Šernek, M. Obućina, M. Kitek Kuzman, Effect of wood content in FDM filament on properties of 3D printed parts, Mater. Today Commun. 14 (2018) 135–140, https://doi.org/10.1016/J.MTCOMM.2017.12.016.

[608] A.M. Pringle, M. Rudnicki, J.M. Pearce, Wood furniture waste–based recycled 3-D printing filament, For. Prod. J. 68 (1) (2018) 86–95, https://doi.org/10.13073/fpj-d-17-00042.

[609] What Material Should I Use For 3D Printing? – Advanced Materials Review 1 – BendLay, Laywoo-D3 and LayBrick. http://3dprintingforbeginners.com/3d-printing-materials-bendlay-laywood-laybrick/. (Accessed 16 September 2019).

[610] Wood fiber 3D-Printer Settings, Hestay https://www.hestay.nl/en/3d-print-support/3d-printer-setting-per-material/wood-fiber/. (Accessed 16 September 2019).

[611] Technical Data Sheet Fibrolon® V 135002, Mega 3D. http://media.mega-3d.it/SMDS/colorfabb/Woodfill-TD_FIBROLON_V_135002_en.pdf. (Accessed 16 September 2019).

[612] Technical Data Sheet Fibrolon® V 143301, Mega 3D. http://media.mega-3d.it/SMDS/colorfabb/Bamboofill-TD_FIBROLON_V_143301_en.pdf. (Accessed 16 September 2019).

[613] Technical Data Sheet Fibrolon® HP 7823, Mega 3D. http://media.mega-3d.it/SMDS/colorfabb/Corkfill-TD_FIBROLON_HP_7823_en.pdf. (Accessed 16 September 2019).

[614] C. Scott, 3D printed color-changing material holds potential for information storage, 3DPrint.com (2018). https://3dprint.com/217289/3d-printed-color-changing/ (Accessed 18 September 2019).

[615] Bendlay, filament2print. https://filament2print.com/gb/special-abs/583-bendlay.html. (Accessed 18 September 2019).

[616] K. Plewa, Transparent 3D Printing: what are your options? Sculpteo (2019). https://www.sculpteo.com/blog/2019/11/27/transparent-3d-printing-what-are-your-options/ (Accessed 10 September 2020).

[617] Smartfil Product Guide by smart materials 3D, Smart Materials 3D. https://www.smartmaterials3d.com/en/special-/158-glace.html. (Accessed 18 September 2019).

[618] GLACE Smartfil - 1.75mm, 3D Printers-Shop. https://www.3dprinters-shop.com/en/home/345-glace-smartfil-175mm.html?search_query=GLACE&results=1. (Accessed 19 September 2019).

[619] Technical Data Sheet Smartfil Glace, Smart Materials 3D. https://www.smartmaterials3d.com/en/special-/158-glace.html. (Accessed 19 September 2019).

[620] PLA Rainbow, UniCoFil. http://www.unicofil.de/en/. (Accessed 18 September 2019).

[621] Colour Changing, 3D FilaPrint. https://shop.3dfilaprint.com/reprapper-tech-pla-3mm-blue-green-to-yellow-green-thermochanging-filament-592-p.asp. (Accessed 18 September 2019).

[622] Color change, eSUN. http://www.esun3d.net/products/161.html. (Accessed 19 September 2019).

[623] Color Changing PLA Filaments, 3D Hubs, 2015. https://www.3dhubs.com/talk/t/color-changing-pla-filaments/5929/4 (Accessed 19 September 2019).

[624] D.J. Wales, Q. Cao, K. Kastner, E. Karjalainen, G. Newton, V. Sans Sangorrin, 3D-Printable photochromic molecular materials for reversible information storage, Adv. mater. 30 (26) (2018) 1800159, https://doi.org/10.1002/adma.201800159.

[625] V. Srinivas, Top 5 special filaments for your 3D printer, 3Ding (2018). https://www.3ding.in/blog/top-5-special-3d-printing-filaments/ (Accessed 19 September 2019).

[626] 3D Printing Industry - Worldwide Market Size 2020-2024, Statista Research Department, 2020. https://www.statista.com/statistics/315386/global-market-for-3d-printers/ (Accessed 16 September 2020).

[627] The Complete Guide to 3D Printing Plastic Parts with FDM, Stratasys. https://www.stratasysdirect.com/technologies/fused-deposition-modeling. (Accessed 15 September 2020).

[628] 18 3D Printer Filament Types And Uses, AllThat3D. https://www.allthat3d.com/3d-printer-filament Comparison Guide. (Accessed 15 September 2020).

[629] Complete 3D Printing Filament Comparison Guide, Rigid.Ink. https://rigid.ink/pages/filament-comparison-guide. (Accessed 10 September 2020).

[630] S. Hendrixon, Ultem, PEEK or PEKK? Choosing between high-temperature plastics, Adfit. Manuf. (2019). https://www.additivemanufacturing.media/blog/post/ultem-peek-or-pekk-choosing-between-high-temperature-plastics (Accessed 14 September 2020).

[631] Polyphenylsulfone (PPSU): Techno Brief, Omnexus. https://omnexus.specialchem.com/selection-guide/polyphenylsulfone. (Accessed 14 September 2020).

Further reading

[1] L.N. Ji, Study on preparation process and properties of polyethylene terephthalate (PET), Appl. Mech. Mater. 312 (2013) 406−410, https://doi.org/10.4028/www.scientific.net/AMM.312.406.

[2] Why PEEK material is at the top of its class, Craftech Indus. (2019). http://www.craftechind.com/why-peek-material-is-at-the-top-of-its-class/ (Accessed 14 July 2019).

Images

Ultimaker PP, https://ultimaker.com/materials/pp
PMMA: 3D Printing Materials Overview, https://medium.com/@ZMorph/pmma-3d-printing-materials-overview-140bdd20685a
Ultimaker PVA, https://ultimaker.com/materials/pva
ASA, https://fillamentum.com/collections/asa-filament/
Ultimaker Nylon, https://ultimaker.com/materials/nylon
Nylon FX256, https://fillamentum.com/collections/nylon-filament/nylon-fx256-filament/
About B-PET, https://bpetfilament.com/
PETG, https://fillamentum.com/collections/petg-filament/?
TPU 3D Printing: A Guide to 3D Printing Flexible Parts, https://amfg.ai/2018/07/23/tpu-3d-printing-guide/?cn-reloaded=1
ULTEM™ (PEI), https://3dgence.com/filaments%20/ultem/
PEEK, https://3dgence.com/filaments/peek/
PEKK, https://3dgence.com/filaments/pekk-a/
3D Printer Metal Filament: The Basics & Best Brands 2020, https://all3dp.com/2/3d-printer-metal-filament-basics-best-brands/
Electrically Conductive Composite PLA https://www.proto-pasta.com/products/conductive-pla
Fusion3 F410 Sample Print: 24 Tooth Gears using Carbon Fiber Nylon, https://www.fusion3design.com/fusion3-f410-optimized-carbon-fiber-3d-printer-2/
Desert Tan NylonG Glass Fiber Filament - 1.75mm (3kg), https://www.matterhackers.com/store/l/nylong-glass-fiber-filament/sk/M1XGVZR1
Philament Glass Reinforced, https://filaticum.com/en/product/philament-glass-reinforced/
LAYCERAMIC, http://lay-filaments.com/
LAYBRICK, http://lay-filaments.com/
BENDLAY, http://lay-filaments.com/
3D Printing with Bamboo Wood Filament, https://learn.adafruit.com/3d-printing-with-bamboo-wood-filament
ColorFabb CORKFILL - 1.75mm, https://filaments.ca/collections/3d-filaments/products/colorfabb-corkfill-1-75mm
GLACE, https://www.smartmaterials3d.com/en/glace-filament
Smartfil GLACE, https://filament2print.com/gb/special-pla/1051-smartfil-glace.html
Glow in the Dark PRO Series PLA Filament - 1.75mm (1kg), https://www.matterhackers.com/store/l/glow-in-the-dark-pro-series-pla-filament-175mm-1kg/sk/MYLZV3HN

CHAPTER

15

Polymer powders

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15.1 Powders – introduction

3D printing powder technologies have been used since the mid-1980s, when the first laser technology for sintering polymer powders—selective laser sintering (SLS)—was invented [1–5]. Over the last few years, there has been a dynamic development of machines for the additive production of models using powder 3D printing technologies. Due to the continuous development of material chemistry, as well as the dynamic increase in the demand for prototype production, more and more 3D printing technologies use the input material in the form of powder. A powder is a material in the form of a solid body with a specific grain size, which allows the grains to move freely and continuously adjust them to the shape of a given container. It is this feature that makes many 3D printing technologies use the input material in the form of a powder as a building material [6]. The powder adapts to the shape of the building chamber, and in the event of thermal deformation, it is able to move freely, which prevents deformation and allows the correct sintering process and the laying of the next layer. It is also important to facilitate the cooling process of models after printing. An exemplary photo showing the material spreading method in the laser technology of selective sintering of polyamide powders—SLS—is shown in Fig. 15.1. An additional advantage of powdered materials for 3D printing is the ease of removing models from the build platform. After the construction process is completed and adequate cooling is carried out, the model is removed from the build platform by its removal, without having to be separated from the build platform, as is the case with many 3D printing technologies such as fused deposition modeling (FDM), polyjet matrix (PJM), selective laser melting (SLM), etc. Removing the powder is almost immediate, and in the case of complex models, it is enough to use a compressed air washer, which removes the remains of the powder by reaching the inside of the models. In the case of 3D printing technology, but using metal-based powders, the supporting elements and the model itself must be removed from the building platform by machining, for example, with a saw [7]. This makes it necessary to create additional processing allowances, which is not required in the case of polymer powders such as those described in the presented chapter, and is an unquestionable advantage of the mentioned technologies.

However, the greatest advantage of using powder in 3D printing is the ability to create models of geometry impossible to obtain using conventional technologies. By using the supporting material in the form of a powder, we can create geometries in which the supporting material can be removed by gravity (poured out) (Fig. 15.2). In addition, powder that has not been sintered can in many cases be reused after sieving and mixing with fresh by using an appropriate vibrating and mixing chamber (Fig. 15.3). However, the refreshing process can be performed only to a limited extent and usually does not exceed 50% of the used material mixed with fresh, new powder. This process does not apply to 3D printing technologies using metal-based powders because in many cases it is possible to reuse almost 100% of the same powder, if it has not melted. In the case of plastics and the stage of refreshing the powder mixture is omitted, the model made will be characterized by lower dimensional and shape accuracy and lower mechanical and visual properties. In addition, the used material is characterized by a different value of shrinkage during the process of both building and cooling, which affects the thermal stress and, consequently, the deformation of the constructed model and its dimensional and shape accuracy.

Polymers for 3D Printing
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FIGURE 15.1 Selective laser sintering printing platform (Formiga P100 machine); material—polyamide PA 2200.

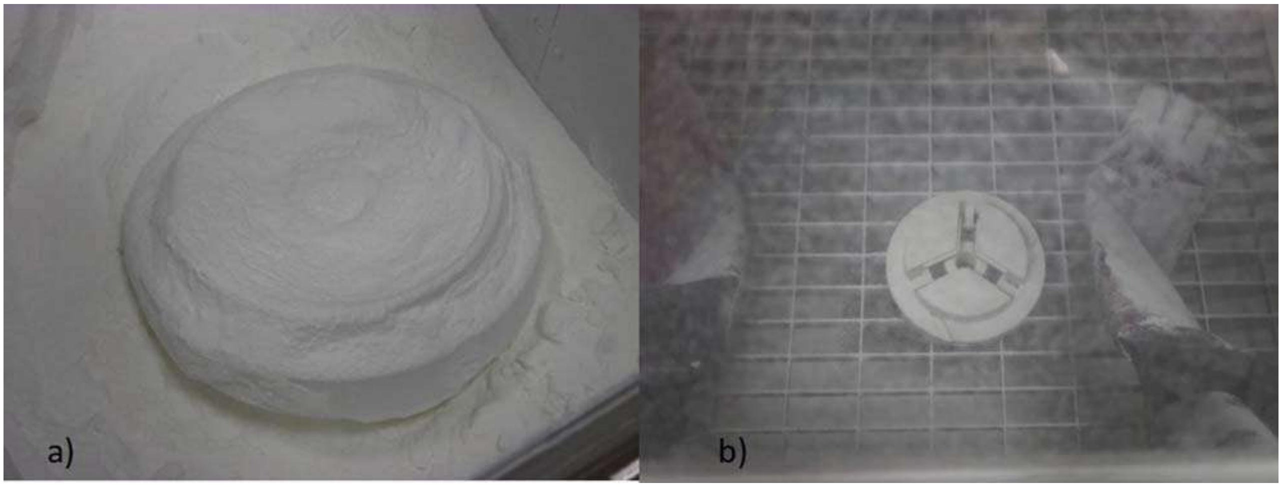


FIGURE 15.2 Cleaning the model in powder technology: (A) gravity, (B) using compressed air.

FIGURE 15.3 The process of screening and mixing the used and fresh powder using a vibrating agitator.

Compared to many other 3D printing technologies in which the supporting material is in the form of, for example, a solid or liquid polymer resin, in the vast majority of cases it must be removed mechanically or chemically, which limits the use of these technologies and reduces production flexibility and adversely affects the quality of the obtained surface and, consequently, for example, the tribological wear of models [8]. Fig. 15.4 [9] shows a model made with the use of three 3D printing technologies with a different type of creating support structures. In the case of Fig. 15.4A, black support material is clearly visible. This model was made in the fused deposition modeling technology of ABS (acrylonitrile butadiene styrene) material. This material can be removed either mechanically or using an ultrasonic cleaner. In the case of mechanical removal, however, one should take into account the damage to the surface of the model resulting from the process of removing the supporting material, or scratches on the surface resulting from the use of sharp tools. If an ultrasonic cleaner is used, the material must be chemically treated with liquid chemical compounds, which has a negative impact on both its dimensions and functional characteristics such as strength or tribological wear. Another example of a model made this time, however, using the photohardening technology of liquid polymer resins (PJM) is shown in Fig. 15.4C. In this case, the internal channels shown in the drawing are filled with a support material in the form of a polymer resin, which can be removed either mechanically with the use of hand tools or with the use of a pressure washer, in which the liquid under the pressure is fed to the nozzle and manually controlled allows flushing the supporting material. However, both cases of removing the support material have great limitations. First of all, this applies to models with a complex structure, where both hand tools and a nozzle with a pressurized liquid are not able to reach and remove or wash out the supporting material. In addition, too high pressure of the water can damage the outer surface of the models and deteriorate its quality, which is even more painful as the PJM technology is considered to be one of the most accurate 3D printing technologies that uses materials based on liquid polymer resins. The last model shown in Fig. 15.4B was made with the use of powder additive technologies. The model is easy to remove and clean, thanks to the use of powder support material. The support is removed either manually or with compressed air under low pressure. This type of support removal does not affect the geometric structure of the surface and, what is very important and worth emphasizing, allows for the production of thin-walled elements with a wall thickness of about 1 mm, which in the case of additive technologies where the support material must be removed mechanically is impossible to obtain. It is worth emphasizing that the use of powder as a supporting material does not require the use of separate nozzles, as is the case in FDM or PJM technology; on the contrary, it simplifies the construction process and speeds up production.

3D printing technologies that use powdered plastic as input material are one of the most widely used rapid prototyping methods. The laser technologies based on powders include such methods as: SLS of polyamide powders (EOS and 3D systems), HP's Jet Fusion, Voxeljet AG, CJP Technology (3D Systems), SLM (SLM Solution), Beams LDM Systems, Arcam's Electron Beam Melting, DMG MORI's Hybrid AM, ExOne's Digital Part Materialization, Renishaw's AM Systems, laser engineered net shaping (LENS), and direct metal printing (DMP). The first three—SLS, HP, and Voxeljet—technologies use materials based on plastics, where polymers constitute the largest group of materials used, especially enriched with additives. There are a number of methods of classifying plastics (polymers). One is to adapt the approach of using their response to temperature (thermal treatment) and to divide them into thermoplastic and thermosets. In the case of powders, we mainly focus on thermoplastics [10], where their main feature is the possibility of multiple processing, which, however, in many cases requires mixing the old powder with the new one.

FIGURE 15.4 Printing of models from materials in the form of: (A) solid, (B) powder, (C) liquid (resin).

Further in the chapter, in Sections 15.2–15.7, the properties of materials based on plastics used in well-known 3D printing technologies—SLS and HP Jet Fusion [11]—and occurring in the form of a powder are presented. In particular, attention has been paid to the well-known materials based on polyamides (PA) from the group of PA 12 polyamides enriched with additives.

The principle of model construction in technologies such as SLS and SLM is shown in Fig. 15.5. In the HP Jet Fusion (HP MJF) technology, polyamides PA 12 are the main building materials, and thanks to the possibility of controlling technological parameters, it is possible to create new materials, add additives to the existing ones, and obtain mixtures with new, unique properties. Due to the fact that this is a relatively new technology, it has not been subjected to as many tests as is the case with powder sintering in SLS technology. Moreover, an analogous situation applies to the formation of new powder mixtures, which have also not been sufficiently well described in the literature so far. In the HP MJF technology, the material in the form of a powder is delivered to the building chamber and distributed in the place of the currently built layer, then the machine applies drops of a special agent with thermal properties and responsible for melting the powder (to fuse the layer) in the place of the currently built layer of the cross section of the model. After the process is complete, the build platform is lowered by the appropriate amount and a new layer of powder is spread. After completion of the construction process, the platform undergoes a process of cooling and cleaning of powder residue that has not been sintered and which served as a support. Also in this technology, the powder is reused.

The powder used in laser technologies is distributed either through the distributing roller or through the distributing arm. In the case of a powder with a high density and also a high build temperature, a very important factor is the correct positioning of the models on the build platform. The printing direction is the key technological parameter influencing the metrological, mechanical, and tribological properties. As can be seen in Fig. 15.6, the same model can be positioned in several variants relative to building plane (in figure—XZ) on the build platform, which ultimately translates into a different layer arrangement in the model, the number of layers, construction time, and cooling down process, and consequently a number of anisotropic properties.

Analyzing scientific publications [1,12–21] on the influence of technological parameters on the properties of models produced with powder technologies from polymer-based materials, it can be clearly stated that the print direction is a key parameter influencing almost all properties of the models produced. As shown by numerous scientific publications on not only polyamide powders but also steel, depending on the printing direction, the roughness,

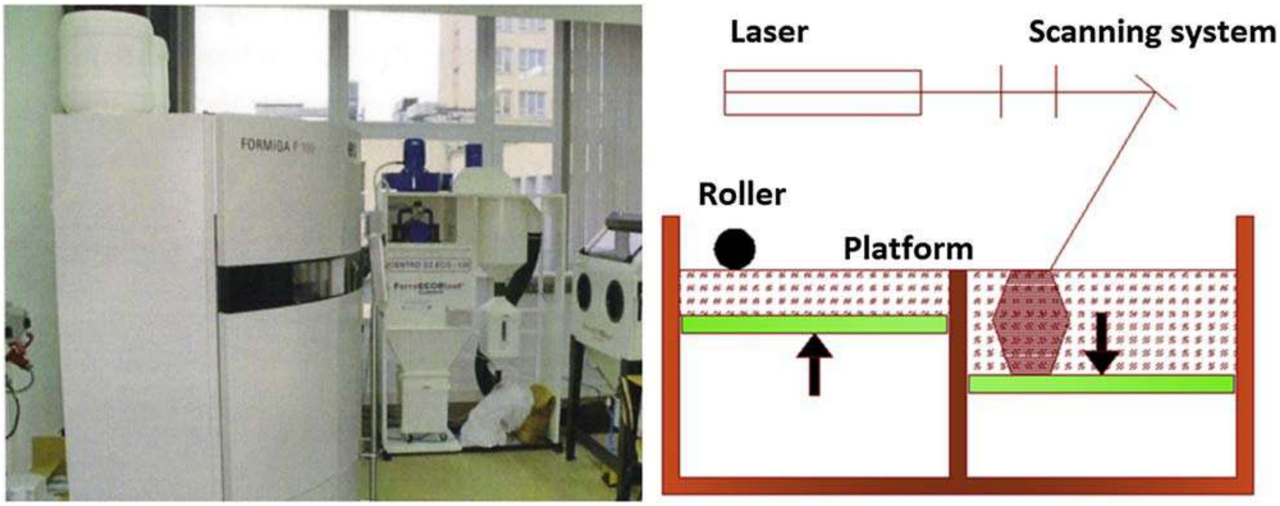


FIGURE 15.5 Diagram illustrating the principle of building models using laser 3D printing technologies: in this case SLS.

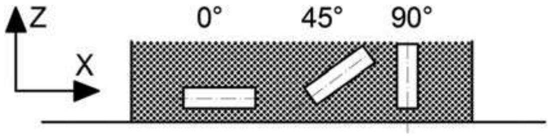


FIGURE 15.6 Printing of models from materials in the form of powder, in various variants of positioning the models on the platform in the XZ plane.

and waviness of the surface change, shape errors occur, the strength of the model changes, as well as tribological wear. Especially the last parameter, tribological wear, is very important in the case of using polymer powders to build fully functional models, which are expected not only to be highly accurate and durable, but also to be highly abrasive. Moreover, due to the nature of the layer bonding, the sintered polyamide requires a very careful cleaning process. In some cases, however, despite the cleaning process due to insufficiently good reflection properties, it is not possible to carry out reliable, credible measurements using optical devices. In the case of polyamides based on PA 12 percent of the measurement points that have been measured during optical tests in many cases does not exceed a dozen or so percent; therefore it is necessary to approximate with mathematical programs that do not reflect 100% of the tested surface, but only try to recreate on the basis of known mathematical algorithms. It can be said that 3D printing technologies using polymer materials in the form of powders require a great knowledge, skills, and a wide range of measuring equipment enabling the analysis of the occurring phenomena. The nature of the laser path in the case of sintering polyamide powders in laser technologies is shown in Fig. 15.7, where it can be noticed that in the case of powder sintering, it is very important to have the appropriate grain diameter as well as the appropriate technological parameters for a given polymer, such as: printing direction, thickness layers, the overlap factor of the laser beam (marked with the symbol, h, in Fig. 15.7), as well as the temperature of the building chamber and the type of protective atmosphere. In many cases, a gas such as nitrogen or argon acts as the protective atmosphere.

An important disadvantage of using the powder as both a building and supporting material is the unfavorable phenomenon of the so-called stair-step effect, which results in clear level differences at the interface between the layers, visible without any device. This feature applies not only to 3D printing technologies using powders, but also other forms of material delivery and is mainly related to the layered nature of model construction. The stair-step effect largely depends on the correct saving of stl files and the arrangement of the models on the build platform (Fig. 15.8). In the case of powders, the thickness of the layers is largely dependent on the average size of the powder grains, which determine how large the value of the thickness of the built layer (layer height) can be set. It can be said that the average grain diameter of polyamide powders ranges from 50 to 80 μm. If the layer thickness is too high, the models may break even during the cleaning process or preparation for further testing, as shown in Fig. 15.9. In the case of polyamide powders, the layer thickness is usually around 100 μm, which is a satisfactory value and only photo-curable technologies are able to build models with a much smaller layer height (up to several micrometers), thus reducing the so-called step effect. Due to this fact, you can of course take actions to improve the visual quality of the model. As materials show good machinability, polyamides can be processed by further machining, chemical, and thermal treatment [22].

In the further part of the work (Sections 15.2–15.7), the materials widely used in SLS and HP Jet Fusion technologies for several leading machine and powder manufacturers, including companies such as EOS GmbH, 3D SYSTEMS, and HP, are discussed. The two first leading manufacturers are involved in the construction of machines and provide a wide range of materials enriched with many additives. In addition, selected properties of powdered materials used to build models in HP MJF technology are presented. Due to the fact that both technologies have open chambers with the possibility of set technological parameters and the possibility of their smooth adjustment, it is possible to create new materials with different physicochemical properties.

Summarizing Section 15.1, it should be noted that thanks to the use of the powder as a building material in 3D printing, new possibilities for the construction of prototypes were created and it was possible to very easily create new materials based on polymers, in particular from biocompatible polymers with high strength properties. In addition, it is worth emphasizing that the powder is extremely easy to remove, transport, and store, and the durability of

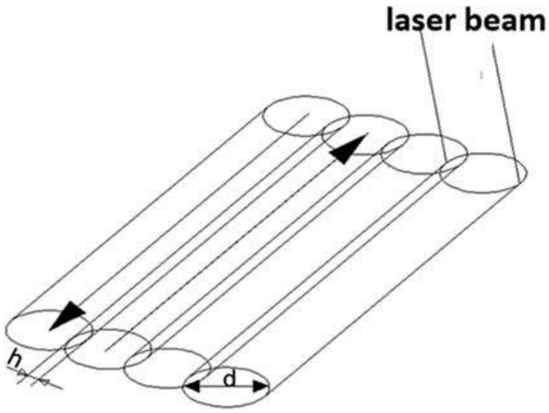
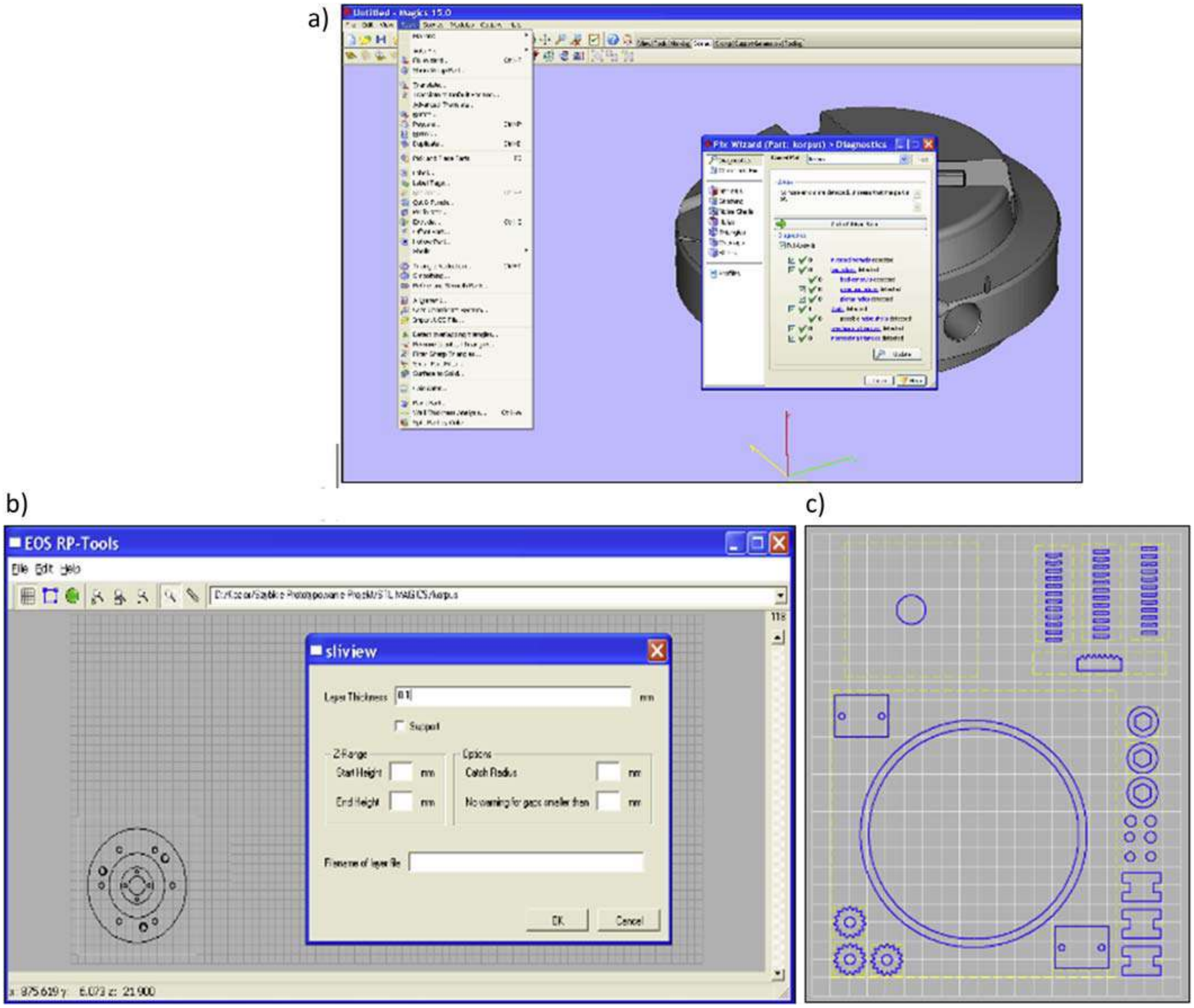


FIGURE 15.7 Diagram illustrating laser paths sintering powdered material in the case of sintering polyamides in laser technologies [9].



Layer Thickness 0.1 mm

FIGURE 15.8 Working with 3D files during production with SLS technology: (A) checking the correctness of approximation of stl files, (B) division of models into layers, (C) arrangement of models on the virtual machine building platform.

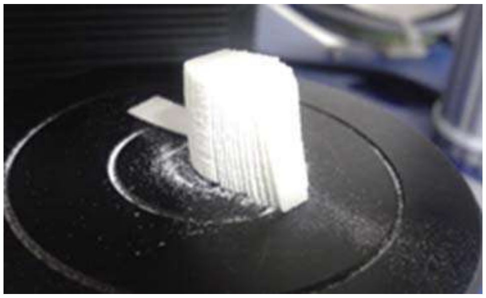


FIGURE 15.9 The model is made in the technology of selective laser sintering of the material PA 2200 (PA 12) with a given thickness of the built layer 0.5 mm [15].

the models produced is similar to those produced by conventional technologies. It is also worth emphasizing that these technologies are still developing, and the very principle of using the powder opens new doors to the use of new polymer materials.

15.2 Polyamide powders

Polyamide known from the end of the 19th century to mass production entered the United States in the 1930s. Polyamides are one of the most commonly used industrial plastics and one of the most frequently modified and enriched materials. This applies to both production with the use of conventional technologies (casting, injection molding, machining) and nonconventional technologies, such as 3D printing technologies (additive/generative technologies). The most common polyamides are: PA 6, PA 6.6, PA 11, PA 12, PA 12 GF (with glass fiber), PA 12 MoS_2, PA 6G + MoS_2 (with molybdenum disulfide), Aramid, Polyphthalamide, and Alumide. Polyamides belong to the group of plastics called polymers, and their characteristic features are amide bonds, which distinguish them from other known plastics. Due to good machining properties, this material can be subjected to turning, milling, and drilling, which significantly affects its large industrial application. Polyamide as a material in 3D printing technologies comes in two forms: filament and powder. Chapter 14.3.3 comprehensively presents the properties of polyamides used in 3D printing, which are solids (filaments) and are used in the FDM/FFF technology. In the Section 15.2 presented, however, we focus our attention on polyamides supplied in the form of powders and used mainly in 3D laser printing technologies.

In the case of polyamides used in 3D printing, they relate largely to mixtures based on polyamide PA 12, which is a well-known construction material. Polyamide PA 2200, which is used in SLS technology in Formiga type systems by EOS GmbH, is based on PA 12 polyamide; however, due to the fact that the printing process is a layered process and the material in printer is a powder, this polyamide can be mixed with many additives, which makes it possible to create new materials by introducing a variety of additives. Additions open up new possibilities for designers to use 3D printers to build prototypes and functional models with versatile possibilities. An example of this can be the more and more considered use of 3D printers, especially when using powders to build models with microelectromechanical systems (MEMSs) applications [23]. Moreover, technologies such as SLS are widely used in medicine in a wide variety of applications [24–26]. In the case of EOS systems, one of the leading producers of both 3D printing machines and powder material, we can use polyamides based on PA 12 polyamide, such as: PA 2200, PA 2201, PrimePart FR (PA 2241 FR), PA 2210 FR, PA 3200 GF, Alumide, and PA 640-GSL and those based on the polyamide PA 11: PA 1101, PA 1102, HP 11-30, and FR-106. Moreover, research is conducted on obtaining new materials by both introducing new additives and mixing the already existing powders in various proportions. It is the latter type of research that has been widely described in several scientific publications [27–31].

The most common polyamide in the processing of plastics is PA 12; in this chapter there are a number of mechanical, chemical, and thermal properties as well as the results of experimental studies presenting this material. In addition, much attention has been paid to presenting the materials in a slightly modified form after the introduction of additives. The description omits the properties of pure PA 12 polyamide, as it is described in detail in Chapter 14. Therefore, the main focus is on polyamides, which, through the use of appropriate additives, exhibit a number of enhanced properties. In the following, the analysis of the properties of materials obtained by introducing additives will be carried out in comparison mainly to pure polyamide PA 2200 (PA 12). In the case of powder technologies that enable the use of polyamides in the form of powders, the leading manufacturers of machines and materials include companies such as: EOS GmbH, 3D SYSTEMS, and HP Jet Fusion. In the further part of the work, the materials used in the SLS and HP Jet Fusion technologies were compared.

The results of the current research on polyamide powders, which are used in 3D laser printing technologies, are focused on many aspects. One of the key research aspects is to assess the quality of the models. Through assessment, scientists most often analyze both the strength of the models produced and their quality. Quality is understood by the analysis of dimensional and shape accuracy and the assessment of the surface layer expressed by the parameters of roughness and waviness (both profile and plane). In the case of strength, the basic parameter is the tensile strength performed during the uniaxial tensile test. During this test we are able to estimate both the Young's modulus and the tensile strength. This does not mean that other tests, such as compression, relaxation, or creep tests, are not performed. Rheological tests largely allow for the evaluation of powders in terms of their real use in the construction of fully functional models that are subjected to continuous loads. In the case of powders based on PA 12 polyamide, the rheological properties depending on the printing direction have been described very well in the works [15,32]. Such tests are applicable to all types of elements of connections, elastic connections, or complex structures with a cellular structure, which are very popular recently. Cell structures are widely used in medicine, as well as wherever appropriate reaction of the material to dynamic loading and vibration damping is required. In the case of SLS technology, polyamide powders are perfect for building the main matrix of the cell structure, which is then filled with a soft material based on, for example, silicones. Research in this direction, concerning this type of structures, was presented in Ref. [33] where the material in the form of a powder was used to build the matrix of the cellular structure.

The results of experimental research on several selected aspects of polyamide powder PA 2200, which is the equivalent of polyamide PA 12, are presented below. The research was carried out as part of the doctoral dissertation of the author of the chapter and during his further research [9].

15.2.1 Assessment of the surface texture quality of PA 2200 polyamide

The study of the surface texture quality of the models began with the assessment of the impact of the basic technological parameters of the SLS technology on the quality of the geometric structure of the surface with the use of polyamide PA 2200 based on PA 12. A machine—Formiga P 100 by EOS GmbH—was used to build the sample models. The analysis was carried out for several variable technological parameters. The selected parameters were: the energy density supplied to the sintered layer of the powder, the value of which was changed in the range of 0.032 J/mm^2 to 0.08 J/m^2, the print direction set at three degrees of variation (0°, 45°, and 90°) in the XZ plane, as shown earlier in Fig. 15.6, and the last technological parameter was the layer thickness (height). The layer height was finally set at two degrees of variation: 0.1 and 0.2 mm. Preliminary studies on the thickness of the layer being built have shown that the already set thickness of the layer being built, 0.3 mm, is so unfavorable that it makes no sense to conduct further research with its use, due to the very poor connection of individual layers. Moreover, with thicknesses of 0.4 and 0.5 mm (Fig. 15.9), the manufactured models almost fell apart when they were removed from the building platform. The models disintegrated into layers, which proves that the previously formed layer was not melted locally and that there was no connection. Tables 15.1 and 15.3 show the results of surface roughness

TABLE 15.1 Surface texture parameters: mean value, Lt – 0.1 mm.

No	Pd, °	Ed, J/mm^2	Sa, μm	Sz, μm	Pa, μm	Pz, μm
1	0	0.032	13.53	108.35	13.18	74.98
2		0.056	13.69	94.60	13.36	77.8
3		0.08	13.64	115.01	13.04	74.69
4	45	0.032	1428	116.47	13.44	76.70
5		0.056	17.26	139.53	16.40	92.98
6		0.08	14.09	106.95	13.44	75.09
7	90	0.032	12.93	101.49	12.58	72.25
8		0.056	14.12	110.73	13.29	77.49
9		0.08	14.55	117.37	13.98	79.12

TABLE 15.2 Statistical calculation of measurements, Lt – 0.1 mm, degree of variation.

No	Sa, μm		Sz, μm		Pa, μm		Pz, μm	
1	12.380	14.688	100.871	115.822	12.337	14.013	71.653	78.299
2	11.338	16.045	20.932	168.265	10.900	15.817	70.996	84.604
3	12.148	15.126	75.169	154.857	11.012	15.068	62.654	86.730
4	8.558	19.993	105.935	126.999	7.385	19.494	57.779	95.612
5	13.060	21.456	98.915	180.139	12.535	20.273	72.517	113.440
6	10.524	17.653	66.807	147.090	10.024	16.864	52.670	97.487
7	11.353	14.497	94.220	108.766	11.516	13.652	68.744	75.758
8	11.751	16.491	67.972	153.493	11.403	15.166	63.405	91.570
9	13.139	15.970	87.522	147.218	12.485	15.476	65.495	92.744

TABLE 15.3 Surface texture parameters: mean value, Lt — 0.2 mm.

No	Pd, °	Ed, J/mm^2	Sa, µm	Sz, µm	Pa, µm	Pz, µm
10	0	0.032	12.96	108.38	12.57	73.44
11	0	0.056	13.18	107.71	12.77	75.89
12	0	0.08	12.02	97.21	11.62	68.08
13	45	0.032	19.94	126.67	19.42	96.46
14	45	0.056	13.67	106.98	13.11	76.01
15	45	0.08	14.45	121.02	13.53	77.69
16	90	0.032	18.71	122.10	18.02	91.49
17	90	0.056	13.71	106.75	13.01	74.29
18	90	0.08	16.1	123.04	15.33	84.88

TABLE 15.4 Statistical calculation of measurements, Lt — 0.2 mm, degree of variation.

No	Sa, µm		Sz, µm		Pa, µm		Pz, µm	
10	11.416	14.513	76.524	140.243	11.381	13.766	64.992	81.896
11	7.937	18.421	60.070	155.344	8.039	17.491	45.572	106.200
12	10.824	13.214	71.098	123.313	10.270	12.967	58.981	77.170
13	10.300	29.575	88.547	164.800	10.003	28.839	66.954	125.961
14	13.531	13.808	81.968	131.999	12.578	13.647	69.364	82.646
15	12.143	16.748	87.946	154.087	11.978	15.085	72.203	83.175
16	10.009	27.403	69.563	174.631	10.041	25.994	58.334	124.649
17	5.763	21.654	26.509	186.985	5.668	20.352	25.283	123.289
18	10.896	21.402	86.874	159.199	10.604	20.051	51.484	118.284

parameters measurements made on cylindrical samples (samples with a diameter of 13 mm and a height of 6.3 mm) made of PA 2200 material. Table 15.1 presents the results for models made with a given layer thickness of 0.1 mm, and in Table 15.3 with given thickness of the layer to be built 0.2 mm. Moreover, Tables 15.2 and 15.4 present the statistical analysis with the indication of the variability range of the test results. Both spatial parameters and parameters of the primary profile (Sa, Sz, Pa, and Pz) were analyzed. The sample model during the tests with the use of the Taylor Hobson CCI profilometer is shown in Fig. 15.10.

Figs. 15.11 and 15.12 show the dependence of the parameters Sa and Sz, respectively, depending on two technological parameters: the printing direction (Pd) and the energy density (Ed). In both cases, the samples were manufactured with a given layer thickness of 0.1 mm.

When analyzing the above Figs. 15.11 and 15.12, certain extremes can be clearly indicated. It is clearly visible that the printing with a given printing direction of 45° and an energy density of 0.056 J/mm^2 is one of the least favorable (the highest rates of Sa and Sz). In the second case (Fig. 15.12) it is also seen that there are two extremes for the highest value of energy density and the 0° and 90° directions. Figs. 15.13 and 15.14 below show the results of measurements of surface profiles and parameters of Pa and Pz (without the filtration process).

Both Figs. 15.13 and 15.14 show very similar characteristics that were visible for the spatial roughness parameters Sa and Sz. Also in this case, the printing parameters for which we obtain the highest profile parameters are the 45° print variant and the use of an energy density of 0.056 J/mm^2. When additionally analyzing the series of measurement results, one can notice the range of variability of measurement results in Figs. 15.15—15.18. They show that in all cases of both the profile and the surface, the variant of the sample number 5, i.e., made with the printing

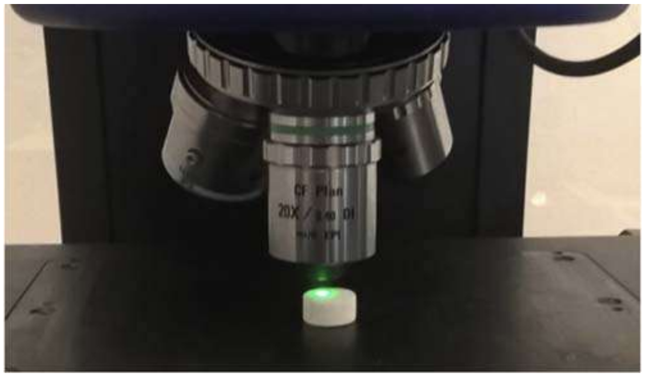


FIGURE 15.10 Model made of PA 2200 polyamide—during testing with the Taylor Hobson CCI optical profilometer.

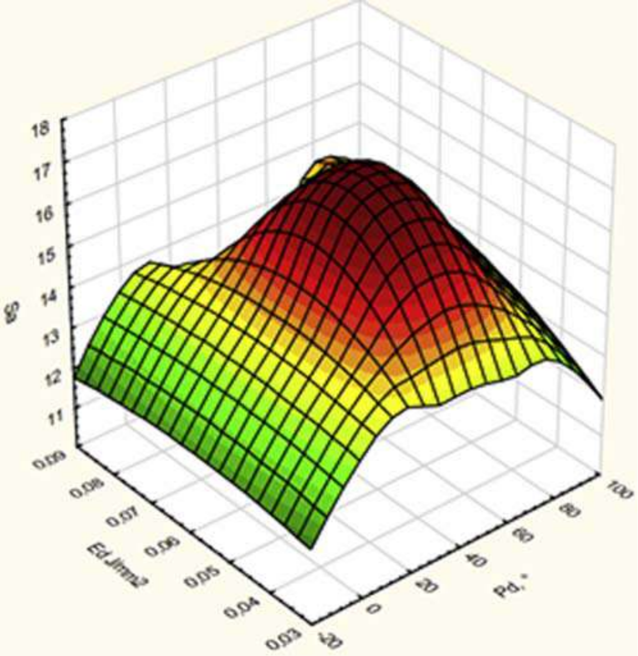


FIGURE 15.11 Dependence of the Sa parameter on variables Pd i Ed (Lt − 0.1).

parameters (Pd = 45° and Ed = 0.056 J/mm^2), is characterized by the least homogeneous measurement results and the highest *degree of variation*. The numbers 1 and 7 can be considered the most homogeneous samples, i.e., those that were made with the given printing direction of 0° and 90°, respectively, and the energy density with the lowest value of 0.032 J/mm^2 in both cases.

Table 15.3 presents the results of surface measurements of sample models made with a given thickness of the constructed layer—0.2 mm. In addition, the table also includes the technological parameters (print angle and energy density). The same measurements of the profile (Pa, Pz) and spatial (Sa, Sz) parameters were made for samples made with a given thickness of the constructed layer 0.2 mm (Figs. 15.19–15.26). Moreover, Table 15.4 presents the results of the static analysis, which allowed for the determination of the ranges of variability of the test results.

Images of the geometric structure of the surface obtained directly from the measuring machine (Taylor Hobson CCI) presented in Figs. 15.27 and 15.28 very well illustrate the so-called stair-step effect. It is particularly visible in the case of the measurement results for samples made with a given print angle of Pd = 45°, which are presented in Figs. 15.27B and 15.28B. You can clearly notice a large number of both peaks and deep valleys. Although the quality of the surface layer, i.e., Pa and Sa parameters, may be at a similar level for all tested samples, the performance properties of details made with such a location on the construction platform will be completely different.

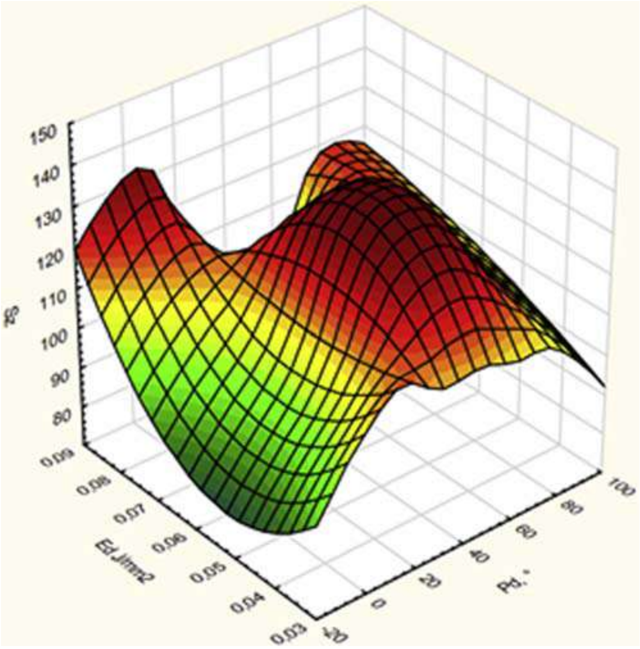


FIGURE 15.12 Dependence of the Sz parameter on variables Pd i Ed (Lt − 0.1).

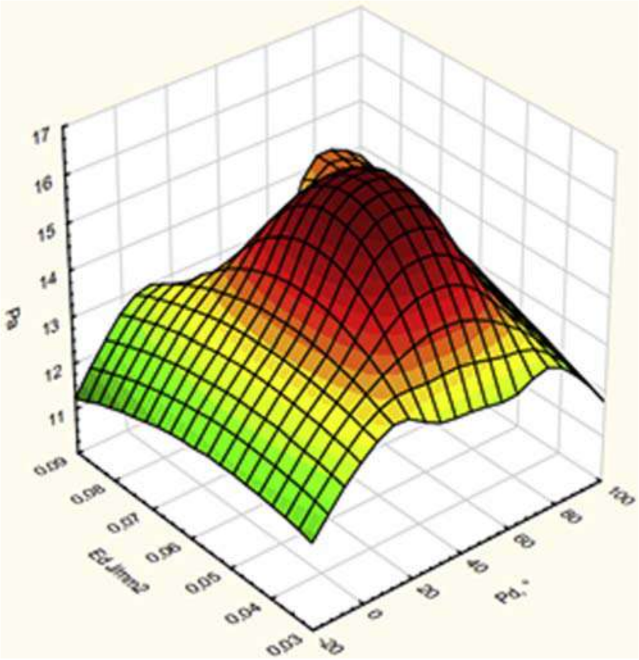


FIGURE 15.13 Dependence of the Pa parameter on variables Pd i Ed (Lt − 0.1).

Considering the presented test results, it can be concluded that the layer thickness, the energy density transmitted to the sintered powder layer, and the direction of "printing" have a large impact on the technological quality of the surface layer of models produced in the technology of SLS and PA 2200 polyamide powder.

In the case of samples made with a given thickness of the built layer of 0.1 mm, the two-dimensional parameters of the primary profile Pa and Pz and the three-dimensional Sa and Sz of the geometric structure of the surface obtain the highest values for the variant of the location of the samples in relation to the building platform at an angle of Pd = 45°. These values are over 25% higher than the other variants of location. Taking into account the energy density parameter and its influence on the geometric structure of the surface, it can be concluded that

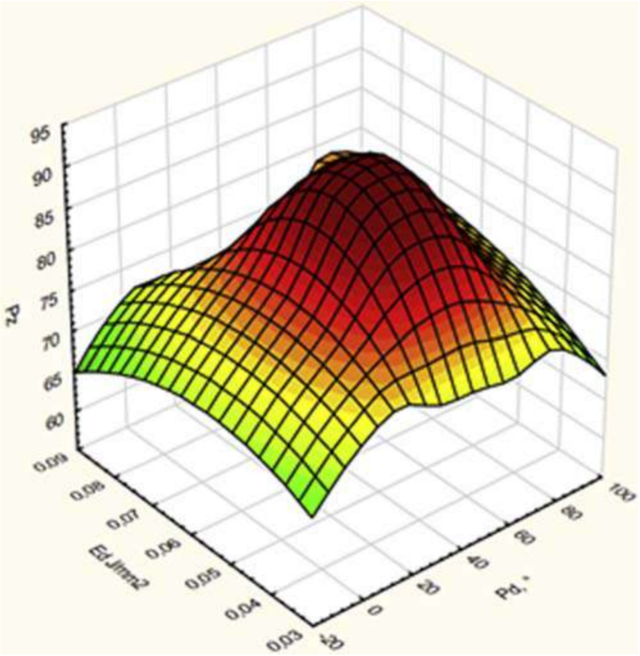


FIGURE 15.14 Dependence of the Pz parameter on variables Pd i Ed (Lt − 0.1).

FIGURE 15.15 Degree of variation Sa, Lt − 0.1 mm.

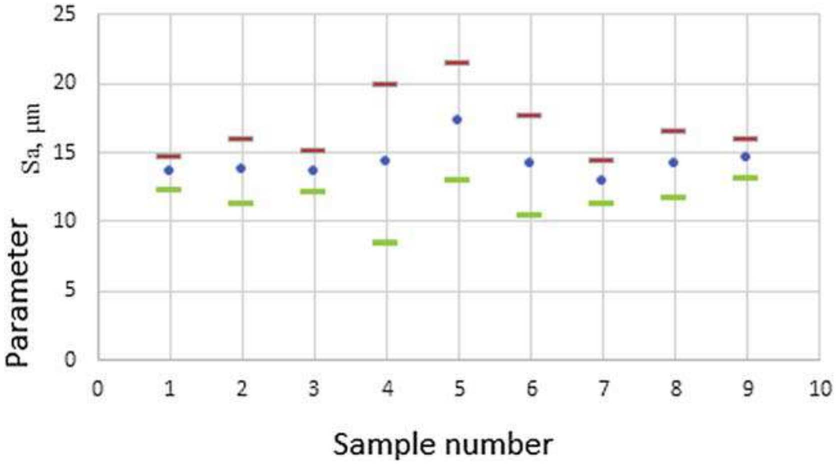
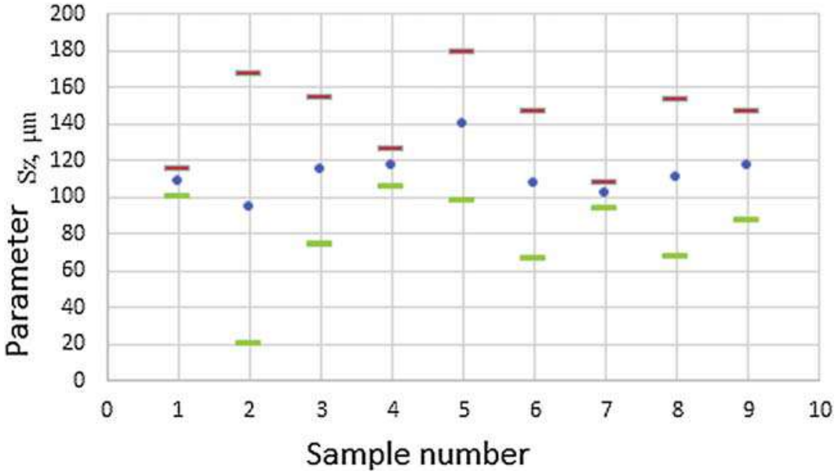


FIGURE 15.16 Degree of variation Sz, Lt − 0.1 mm.



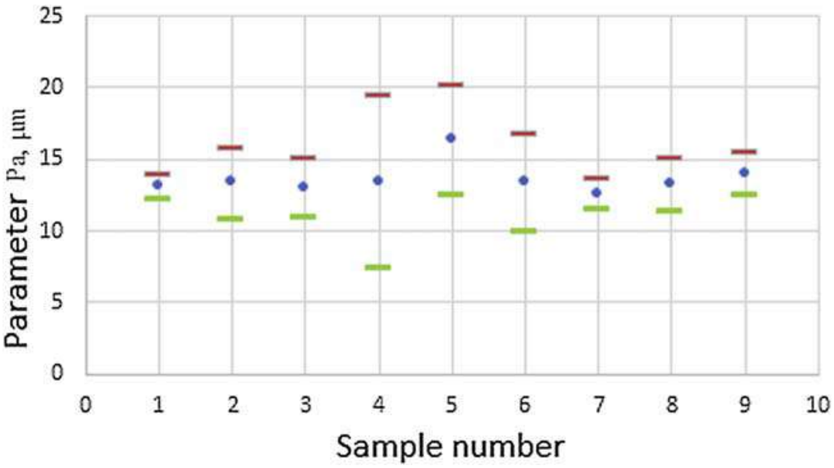


FIGURE 15.17 Degree of variation Pa, Lt – 0.1 mm.

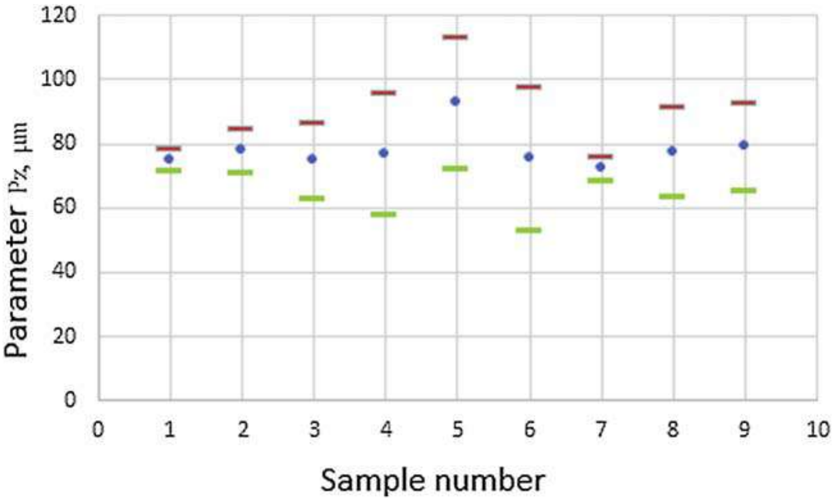


FIGURE 15.18 Degree of variation Pz, Lt – 0.1 mm.

the lowest values of the surface geometric structure parameters are obtained for samples manufactured with the lowest Ed value = 0.032 J/mm^2.

Samples manufactured with a given layer thickness of 0.2 mm are characterized by completely different results of surface parameters. The values of the surface geometrical structure parameters for the printing direction Pd = 0° obtain the lowest values in the case of manufacturing samples with the given energy density Ed = 0.08 J/mm^2. In other cases, i.e., for the angles Pd = 45° and Pd = 90°, the most favorable energy density is the value recommended by the machine manufacturer, i.e., Ed = 0.056 J/mm^2.

15.2.2 Analysis of dimensional and shape accuracy

The dimensional and shape accuracy of models made of PA 2200 polyamide is the subject of many research works. Below are the results of our own research on the analysis of the dimensional and shape deviations of models made of PA 2200 polyamide powder in SLS technology and the Formiga P100 machine. Samples in the shape of a cylinder and a sleeve with the dimensions shown in Fig. 15.29A were designed in the CAD program and then arranged in two selected variants on the 3D printer building platform according to Fig. 15.29B. While maintaining the basic technological parameters recommended by the machine manufacturer (EOS GmbH), i.e., the thickness of the constructed layer 0.1 mm, the energy density transmitted to the sintered powder layer 0.056 J/mm^2, physical models of the samples were made, which were then subjected to the cooling and cleaning process with due care. The view of the samples after cleaning is shown in Fig. 15.30.

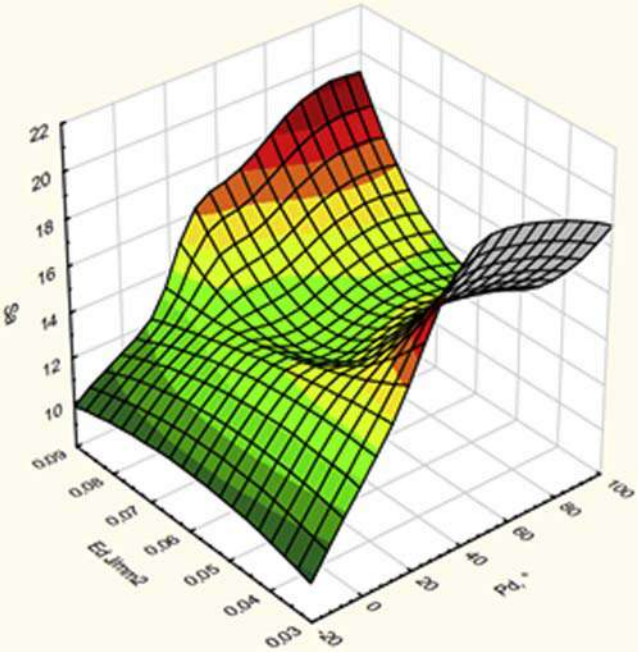


FIGURE 15.19 Dependence of the Sa parameter on variables Pd i Ed (Lt – 0.2 mm).

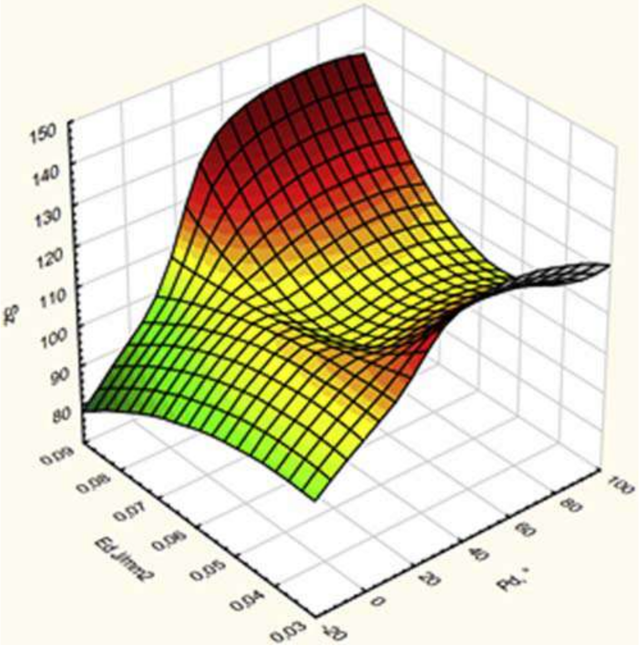


FIGURE 15.20 Dependence of the Sz parameter on variables Pd i Ed (Lt – 0.2 mm).

Table 15.5 shows the dimensions and printing direction of the designed samples. As can be seen, efforts were made to design rolls and sleeves to obtain the appropriate type of fit, assuming the maximum tolerance field. Powder as a building material by irradiation with a laser beam requires the supply of appropriate energy to sinter the layer being built and combine it with the previous one, which means that an area is created around the constructed object in which sintered powder fragments may also appear. It is mainly for this reason that the manufactured models are characterized by shape deviations and dimensional and shape accuracy. The aim of the research was to determine how to design models made of polyamide powder in order to obtain the appropriate accuracy of the manufactured models.

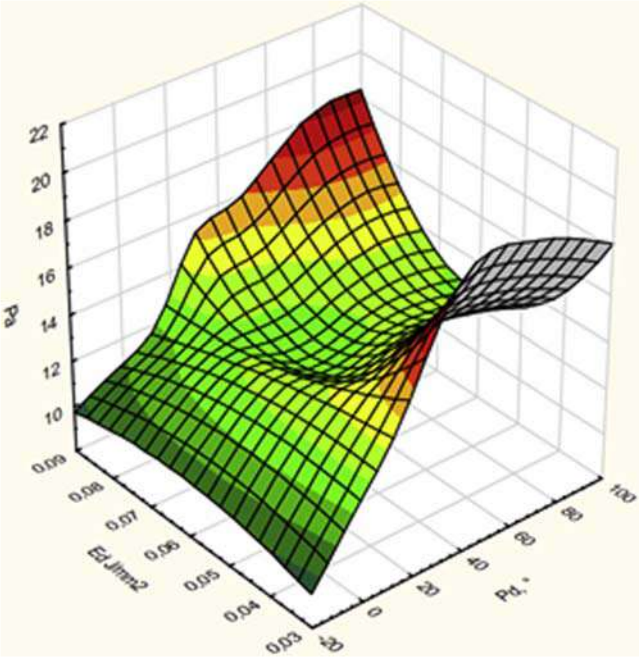


FIGURE 15.21 Dependence of the Pa parameter on variables Pd i Ed (Lt − 0.2 mm).

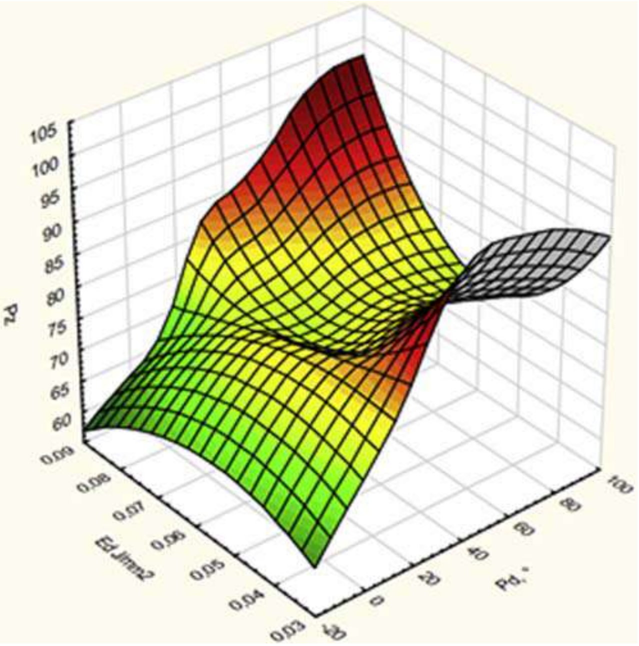


FIGURE 15.22 Dependence of the Pz parameter on variables Pd i Ed (Lt − 0.2 mm).

In Fig. 15.30 you can see the view of the sample models made, the models with numbers 1, 3, 5, 7 were made with a given angle Pd = 90° in relation to the building platforms, and samples marked with the symbol 2, 4, 6, 8 at the angle Pd = 0°.

The tests of the geometrical features of the sample models included the measurement of their diameter and the determination of cylindricity, roundness, and straightness deviations. The primary profile of the tested surface was filtered with a Gaussian filter, thus obtaining a roundness profile in the range of 2−15 waves/revolution. Roundness deviation was determined on the basis of the mean contour (LSCI, also known as Gaussian circle). Measurements of diameters and deviations of straightness were made on the Prismo Navigator coordinate measuring machine by

FIGURE 15.23 Degree of variation Sa, Lt – 0.2 mm.

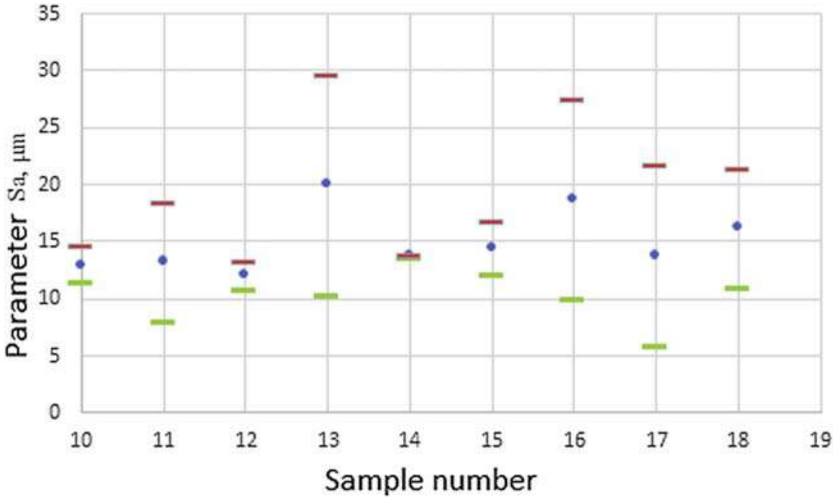


FIGURE 15.24 Degree of variation Sz, Lt – 0.2 mm.

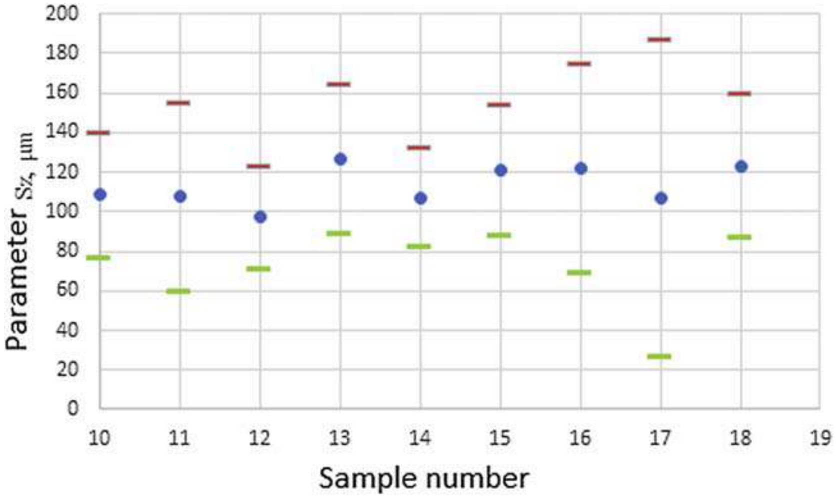
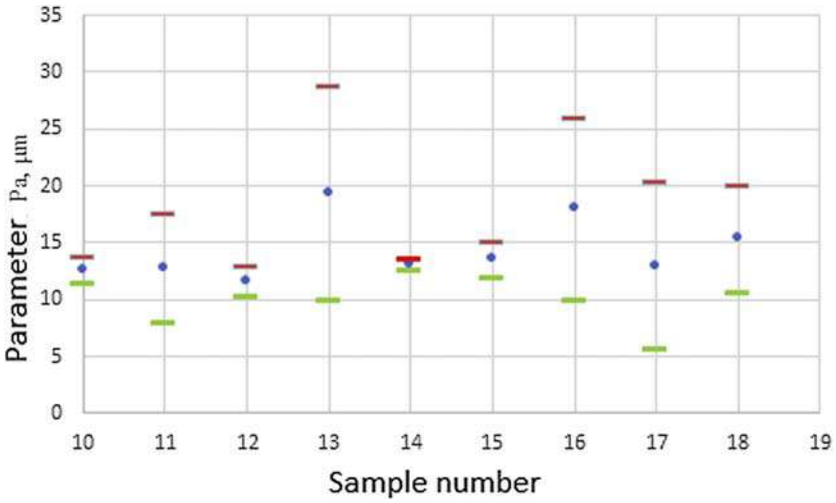


FIGURE 15.25 Degree of variation Pa, Lt – 0.2 mm.



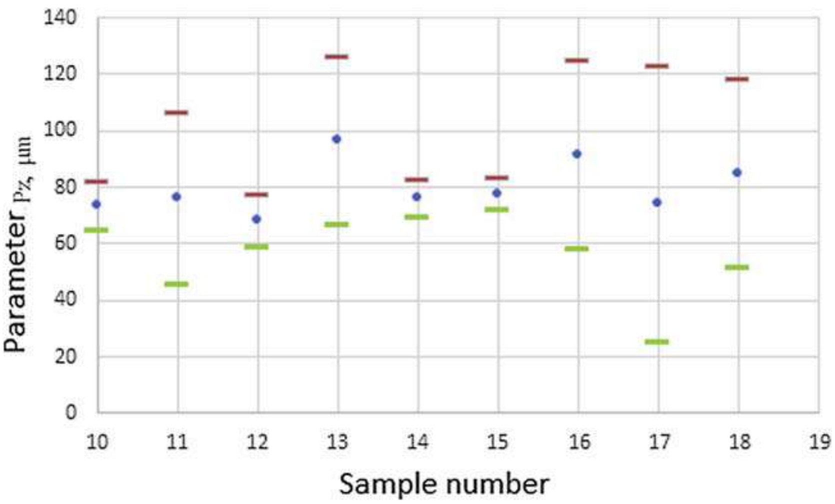


FIGURE 15.26 Degree of variation Pz, Lt − 0.2 mm.

Zeiss with a measuring range of X = 900 mm, Y = 1200 mm, and Z = 700 mm (Fig. 15.31A). The Talyrond 365 machine was used to measure roundness and cylindricity (Fig. 15.21B). Figs. 15.32 and 15.33 show exemplary graphs of measurement of the straightness profile of samples made at two given angle values (Pd). The deviation was measured along the side surface of the cylinder (marked with a thick black line in the graphs).

Figs. 15.34 and 15.35 show exemplary graphs of measuring the cylindricity of the measured sample surface. The determination of the cylindricity deviation consisted in taking measurements in three sections (measurement step = 15 mm) and calculating the mean value.

Figs. 15.36 and 15.37 show examples of graphs of roundness measurements of samples. Measurement was performed at the mid-cross section of both cylindrical and printed sleeve-shaped specimens with preset Pd angles (90° and 0°) for fit e8/H7.

The summary of the results of geometric measurements, i.e., diameters, shrinkage percentage, cylindrical deviation, straightness, and roundness, is presented in Table 15.6. In addition, Table 15.7 and Fig. 15.38 show the statistical analysis of the measurement results.

Based on the measurement results and the calculated technological clearances, it can be concluded that there are significant differences between the dimensions set in digital CAD models and the dimensions measured on physical models. Ultimately, in the physical models of the tested roller—sleeve connection, for any of the presented systems it was not possible to obtain the desired loose.

In the case of physical models of roller, the diameter dimensions were larger than those set in the CAD model by an average of 0.2 mm. Considering the influence of the orientation of the models on the building platform, it can be stated that the more advantageous variant is the location of the samples with a given angle Pd = 90°, which allows to reduce the dimensional deviation by an average of 25% compared to the dimensions of samples made with a given angle Pd = 0°.

The dimensions of the sleeve inside diameters were lower by an average of 0.07 mm for the H7 fit and 0.11 mm for the F8 fit compared to the given CAD dimensions. Finally, the H7/e8 registration index was −0.156 mm for the printing at an angle Pd = 90° and −0.237 mm in the case where the direction was Pd = 0° and for the F8/h6 fits −0.102/−0.158 mm, respectively.

The deviations of cylindricity of the sleeve show significant differences depending on the direction (Pd). The smallest cylindricity deviations were obtained for sleeves made with a given angle Pd = 90°. The cylindricity deviations for the shafts do not show significant differences depending on the orientation.

In all tested sample models, much larger roundness deviations occur when the models are positioned at the Pd = 0° angle during construction, despite the more regular shapes presented in the roundness charts.

The straightness deviation in the case of roller is more than twice smaller for models made with a given angle Pd = 0°, compared to models where the direction was Pd = 90°. In the case of sleeve analysis, there is no influence of the printing direction on the straightness deviation. This allows us to conclude that when models are made with the SLS technology, internal dimensions are much less exposed to the phenomenon of material shrinkage and its dependence on the direction (Pd).

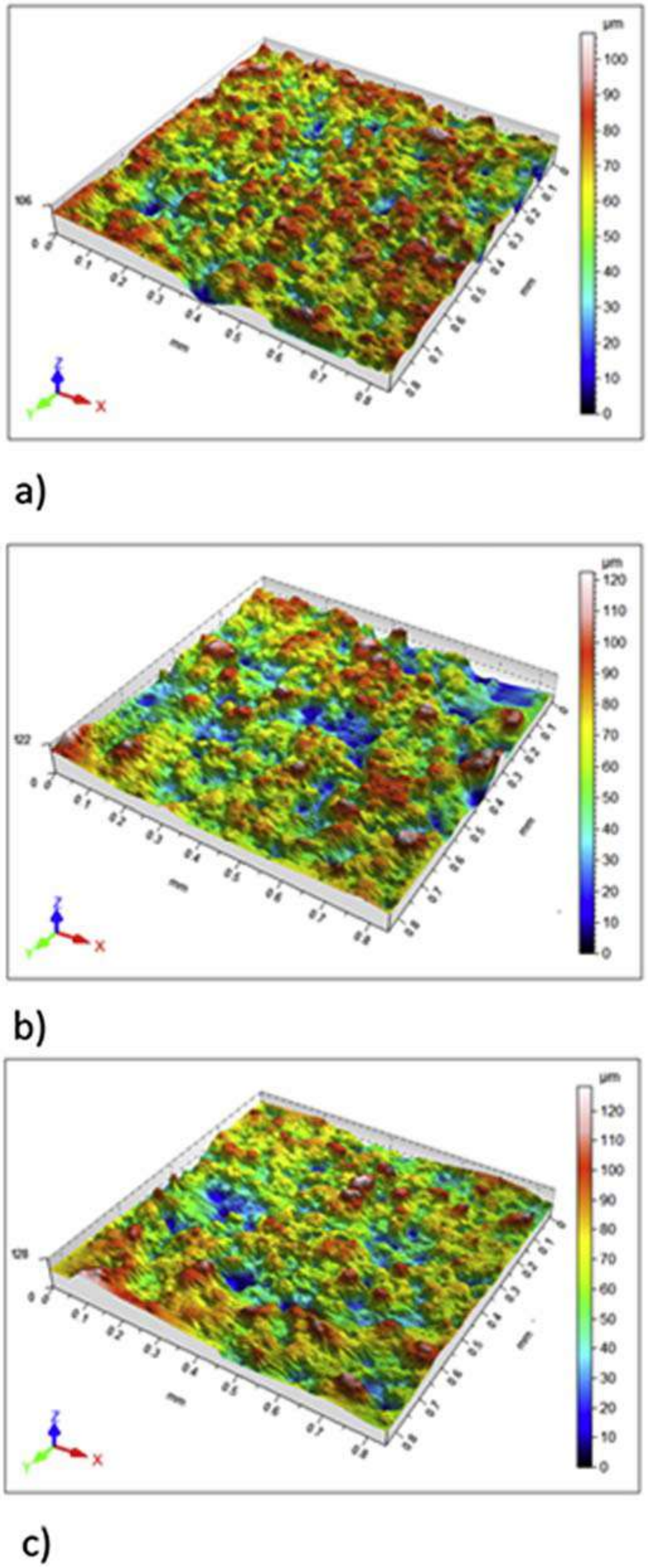


FIGURE 15.27 Surface texture, Lt − 0.1 mm: (A) Pd = 0°, (B) Pd = 45°, (C) Pd = 90°.

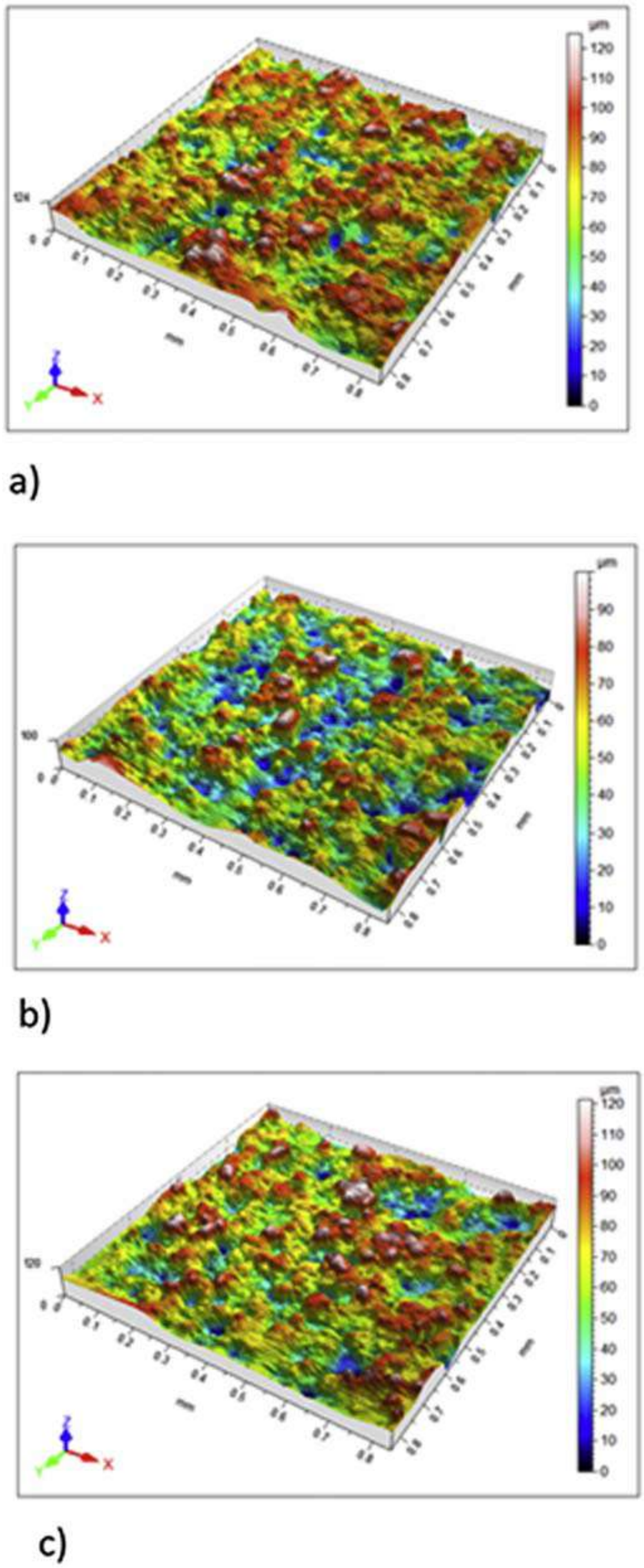


FIGURE 15.28 Surface texture, Lt – 0.2 mm: (A) Pd = 0°, (B) Pd = 45°, (C) Pd = 90°.

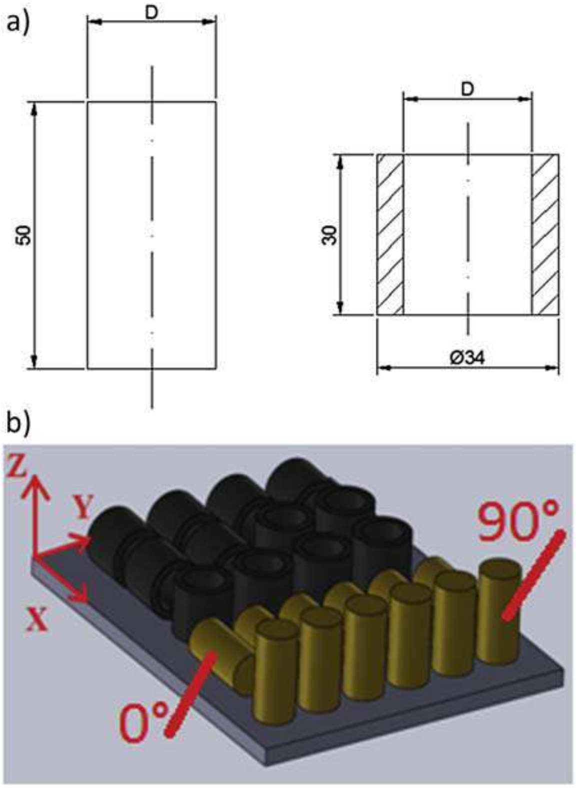


FIGURE 15.29 Tested samples: (A) geometric dimensions, (B) location of CAD models [9].

FIGURE 15.30 Manufactured samples.

The presented research results show that the printing direction has a significant impact on the accuracy of mapping ensuring the required type of fit. Building models without appropriate geometry corrections does not allow to obtain the required fit.

The stair-step effect characteristic for additive technologies is very clearly noticeable for the Pd = 0°, which adversely affects the quality of the surface layer of the cooperating mechanisms and may cause their increased wear. If the tolerance field is too low, an appropriate correction should be made in the 3D model to ensure that the required tolerance field is obtained. This correction should be greater for shafts/Toller (outside diameter), where the geometry mapping error is greater, and smaller for holes, i.e., internal dimensions, where there is less shrinkage.

The process of designing models made with SLS technology should also take into account the deviations of straightness and cylindricity, as well as roundness, the size of which also depends on the printing direction. The presented research results prove that the material shrinkage in the SLS technological process significantly affects the accuracy of the models manufactured, and its value also depends on the dimensions of the model (geometric features).

TABLE 15.5 Samples dimensions.

No	Samples type	D_{CAD}, mm	Pd, °
1	Roller e8	23.927	90
2			0
3	Sleeve H7	24.00	90
4			0
5	Roller h6	24.00	90
6			0
7	Sleeve F8	24.053	90
8			0

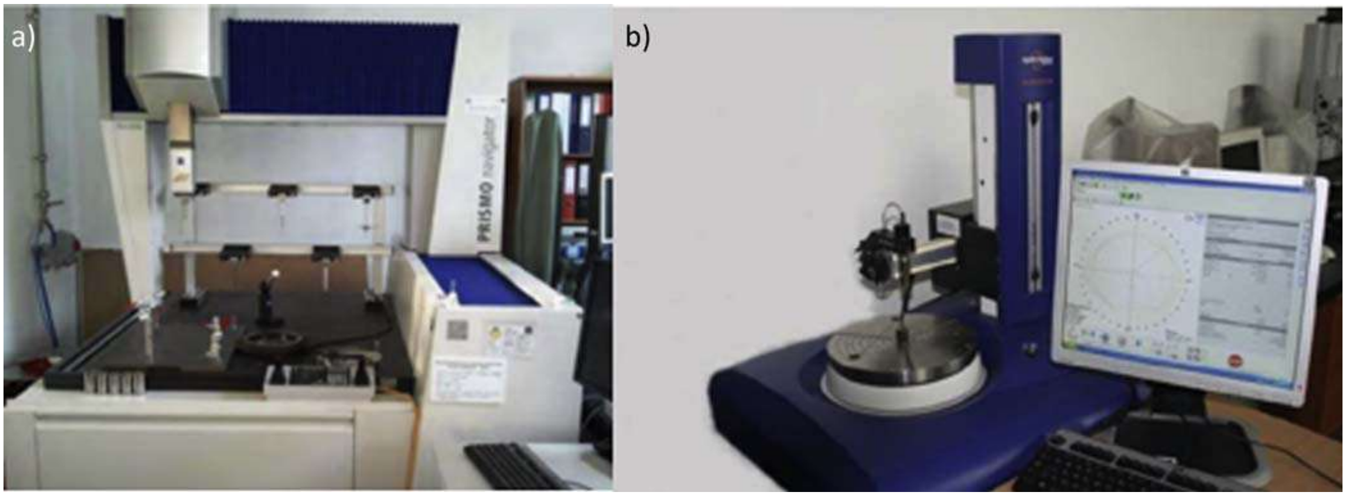


FIGURE 15.31 Measuring machines used in the research: (A) Prismo Navigator, (B) Talyrond 365.

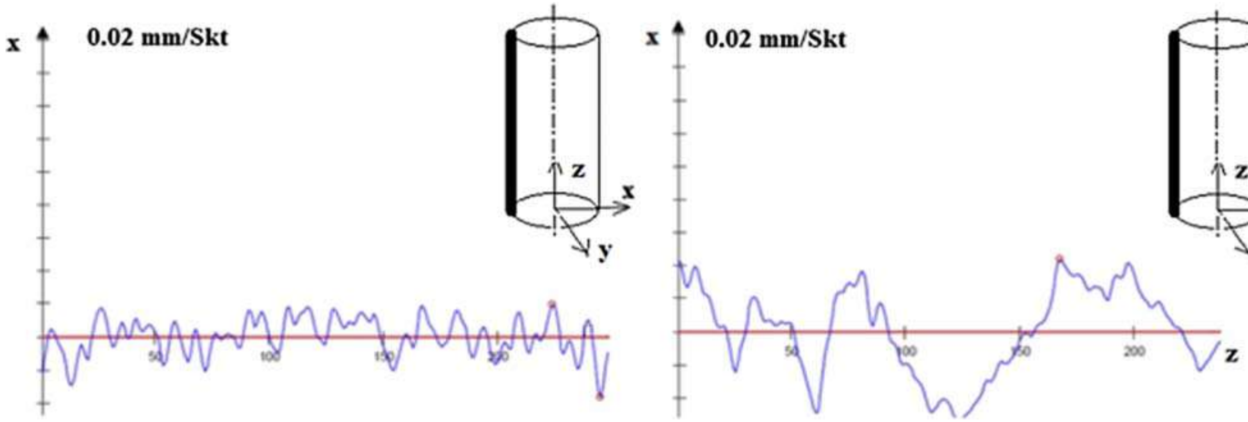


FIGURE 15.32 Straightness profile of roller samples Ø24e8: (A) Pd = 0°, (B) Pd = 90°.

15.2.3 *Polyamide PA 12*

One of the basic polyamides used in the SLS technology is polyamide PA 12. This polyamide as a powder in the SLS technology appears under many trade names, one of them is PA 2200 used in the SLS technology by EOS GmbH. This material has very good properties, selected parameters of which are presented in Table 15.8. This material for printing is prepared in the form of a powder with a grain diameter of 56 μm, which means that models made

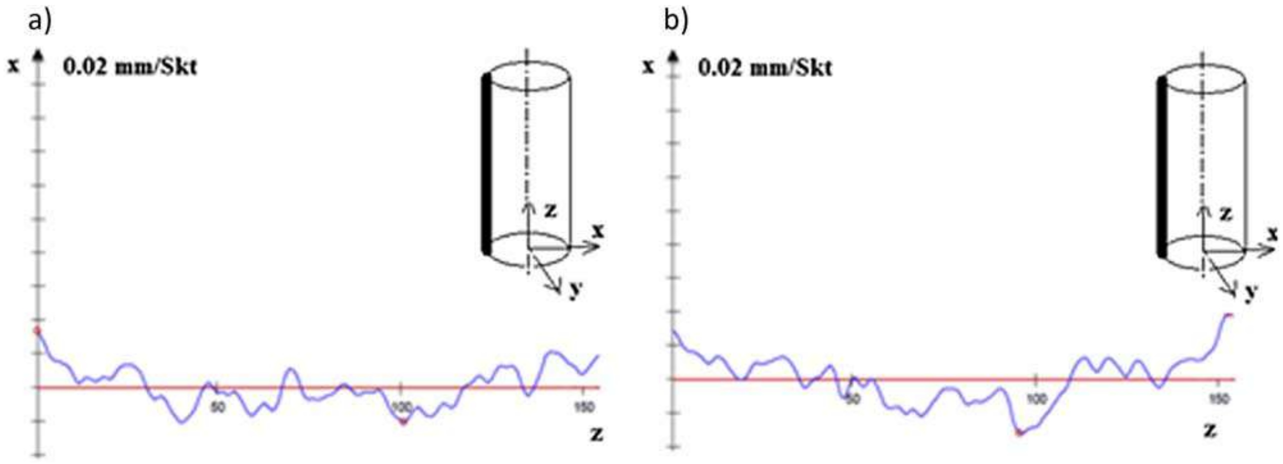


FIGURE 15.33 Straightness profile of sleeve samples Ø24H7: (A) Pd = 0°, (B) Pd = 90°.

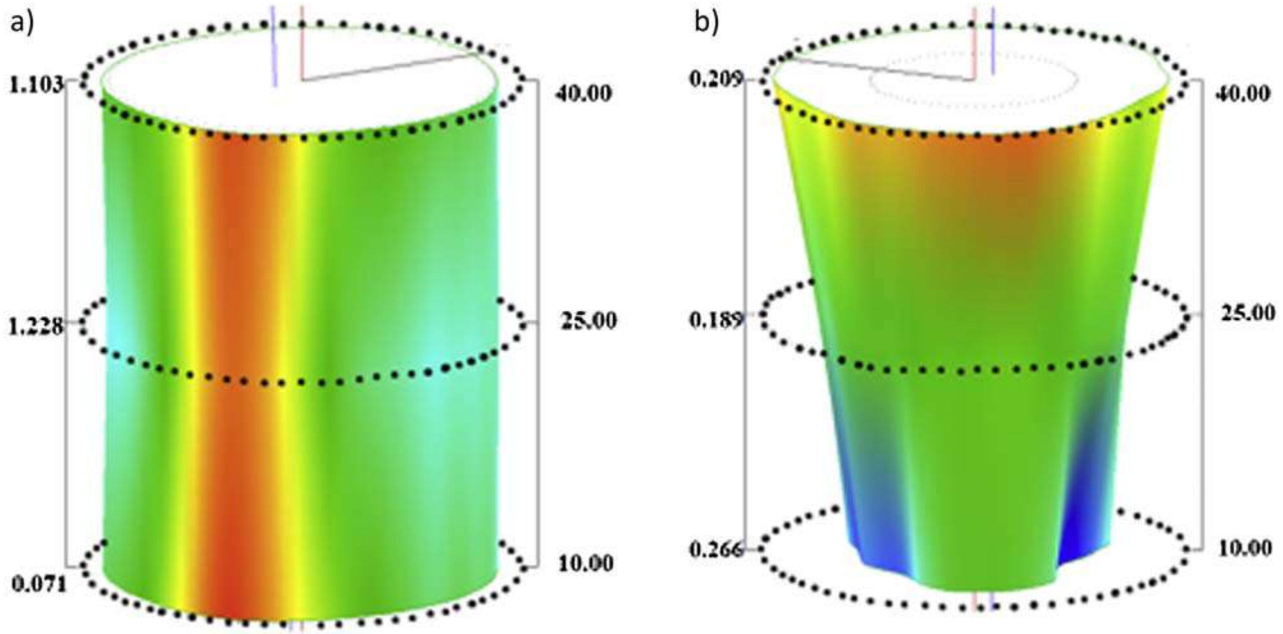


FIGURE 15.34 Graphs of the cylindrical profile of roller samples Ø24e8: (A) Pd = 0°, (B) Pd = 90°.

(printed) from this material can be produced with a given layer thickness of 0.1 mm. This material is one of the cheapest polyamides intended for printing in laser technologies and its finishing treatment has very wide possibilities. In the case of finishing models, you can use painting, polishing, machining, and other forms of improving the surface layer. High hardness determined on the Shore scale also places this material in the group of hard plastics. In the further part of the work, selected examples of creating new models based on polyamide PA 12 (PA 2200) were presented, where the main modification was the introduction of additives increasing selected properties of the manufactured models. Thanks to the additions, the models are characterized by greater durability, lower anisotropy of properties, increased resistance to flammability, and a better weight-to-strength ratio.

15.2.3.1 Polyamide powder in HP jet fusion

Table 15.9 presents the data of the manufacturer of the HP Jet Fusion machine for the polyamide powder under the trade name HP 3D HR PA 12 based on polyamide PA 12. Comparing its properties for the PA 2200 equivalent, which is used in the SLS technology, this polyamide is characterized by a slightly higher density of 1.01 g/cm^3, where the polyamide PA 2200 in the sintered state has a density of 0.93 g/cm^3. When analyzing the strength parameters, it is worth paying attention to the Young's module, which for the polyamide in HP technology has a much

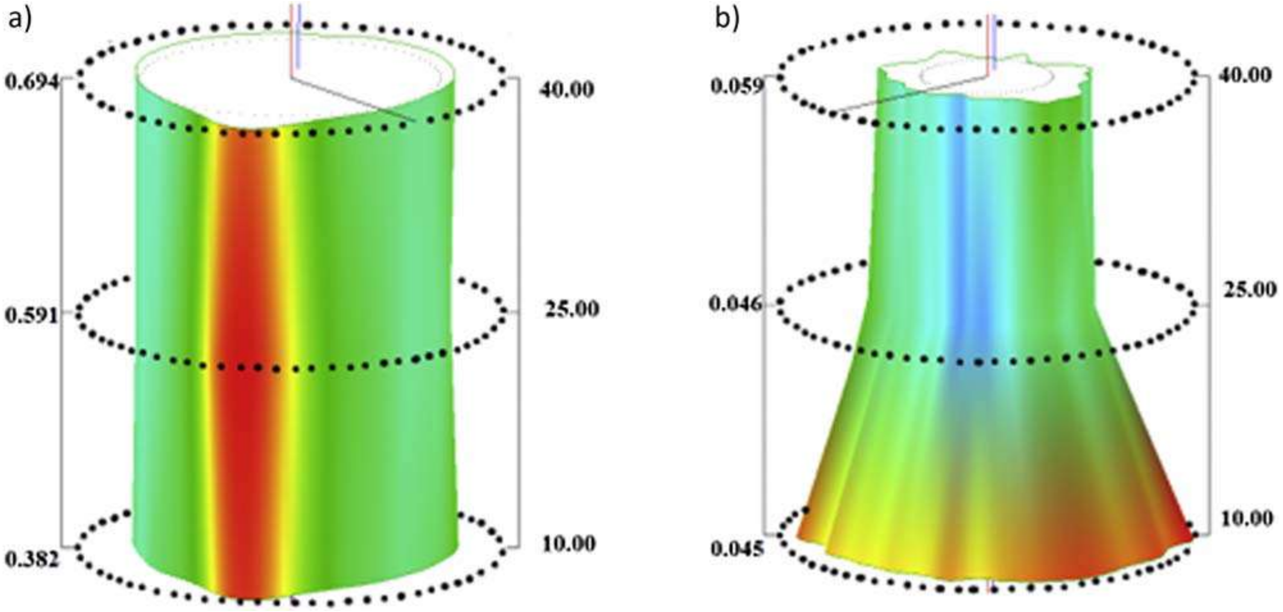


FIGURE 15.35 Graphs of the cylindrical profile of sleeve samples Ø24H7: (A) Pd = 0°, (B) Pd = 90°.

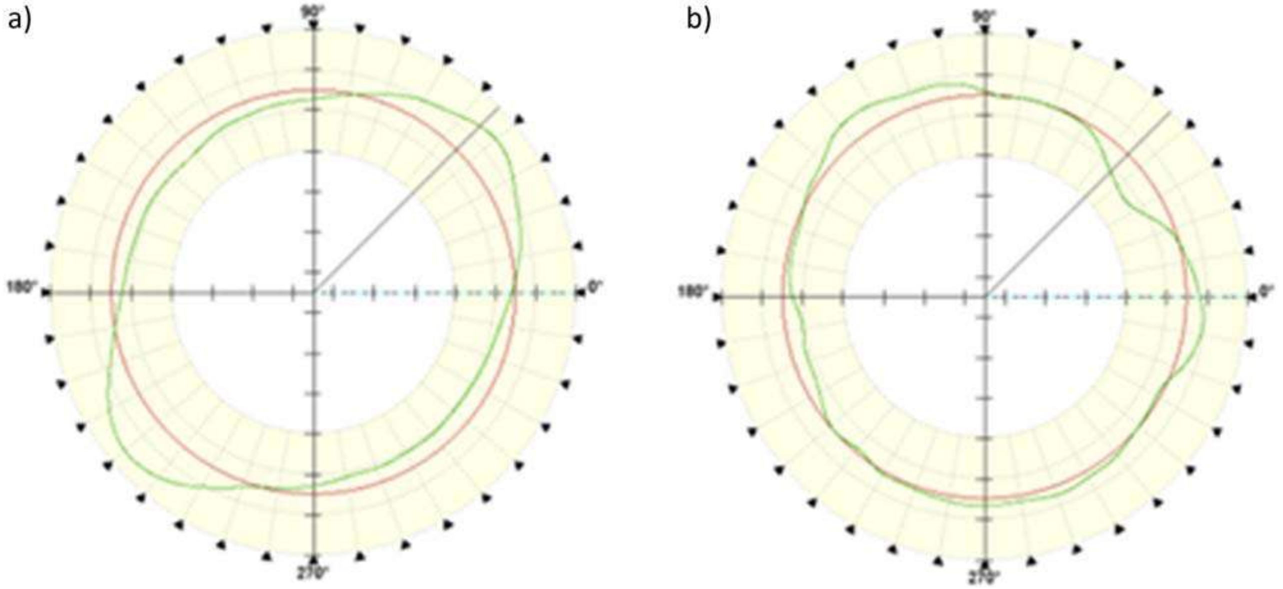


FIGURE 15.36 Roundness profile plots of roller samples Ø24e8: (A) Pd = 0°, (B) Pd = 90°.

higher value of 1900 MPa, by over 200 MPa higher than the polyamide in the EOS technology. The material PA 3D HR PA 12 also shows slightly higher tensile strength, but only by 2 MPa. In the case of polyamide PA 2200 elongation at breast is 24%, regardless of the sample printing direction, which is a much higher value compared to polyamide in HP technology, where these values are 17% for XY printing and 9% for printing along the *Z* axis.

In the case of HP Jet Fusion technology, which is a relatively new technology, there is no large amount of research confirming the properties presented; therefore it is predicted that this material will be of interest to both engineers, designers, and scientists in the future.

15.2.4 Polyamide PA 12 filled with glass beads polymers

One of the most frequently introduced additives increasing the properties, in particular the mechanical properties, of plastics is glass fiber (GF). GF, as evidenced by numerous research results, increases both the mechanical

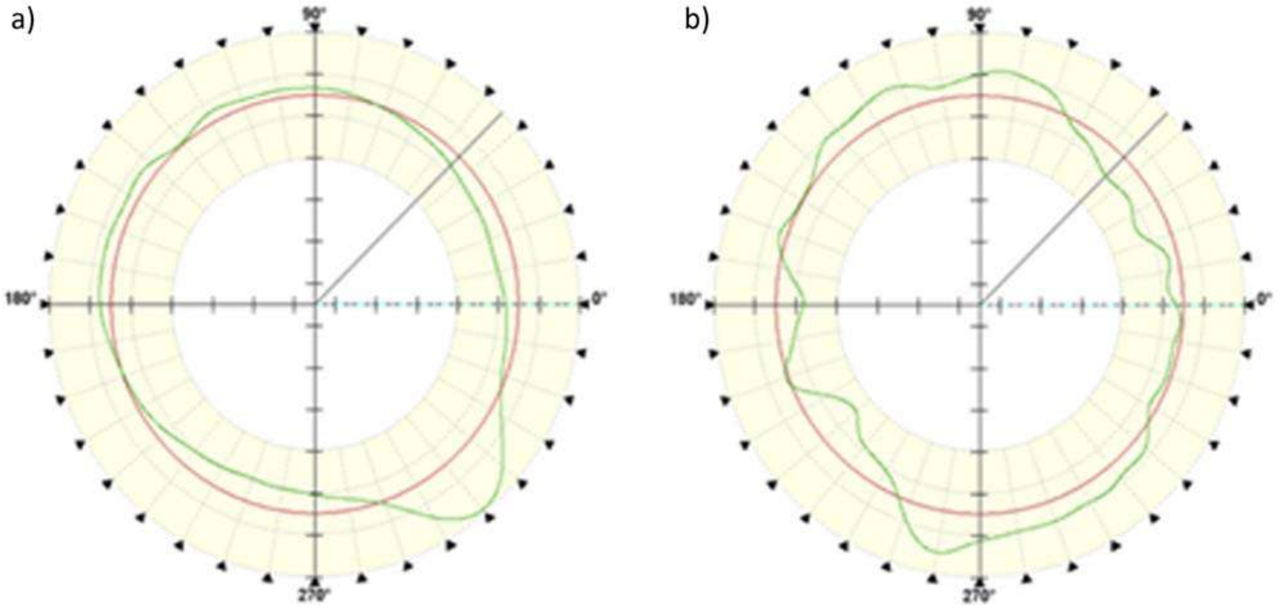


FIGURE 15.37 Roundness profile plots of sleeve samples Ø24H7: (A) Pd = 0°, (B) Pd = 90°.

TABLE 15.6 Measurements results, mm.

No	D_{CAD}	D_R	ΔD	ΔS, %	CYLt	STRt	RONt
1	23.927	24.083	−0.156	−0.65	0.360	0.155	0.119
2	23.927	24.170	−0.242	−1.01	0.332	0.061	0.278
3	24.00	23.927	0.073	0.31	0.095	0.056	0.039
4	24.00	23.932	0.067	0.28	0.409	0.056	0.373
5	24.00	24.155	−0.155	−0.646	0.350	0.144	0.09
6	24.00	24.211	−0.211	−0.881	0.451	0.057	0.360
7	24.053	23.917	0.136	0.565	0.066	0.053	0.038
8	24.053	23.954	0.099	0.412	0.365	0.049	0.333

TABLE 15.7 Statistical calculations.

No	Pd, °	$\bar{x}$	S	U_p	$\bar{x}\pm U_p$	
1	90	24.083	0.121	0.367	23.716	24.450
2	0	24.170	0.026	0.080	24.090	24.250
3	90	23.927	0.035	0.107	23.820	24.033
4	0	23.932	0.014	0.041	23.891	23.974
5	90	24.155	0.042	0.129	24.026	24.284
6	0	24.211	0.009	0.027	24.185	24.238
7	90	23.917	0.018	0.056	23.861	23.973
8	0	23.954	0.019	0.058	23.896	24.012

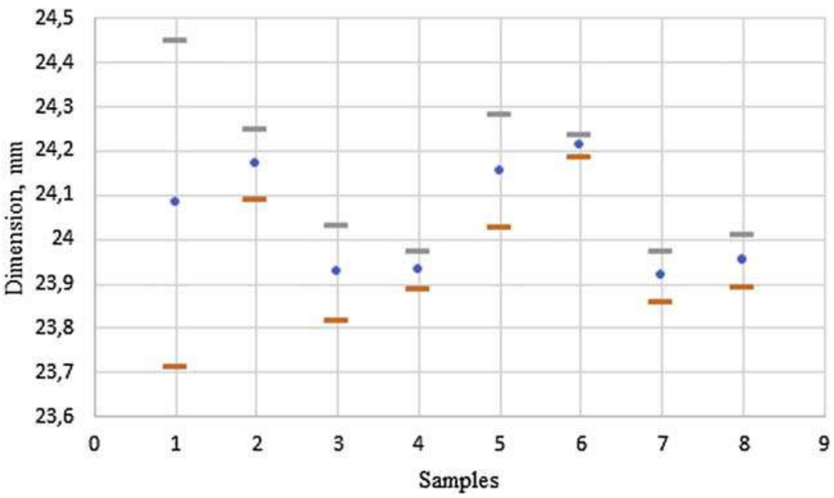


FIGURE 15.38 Statistical interpretation of measurements.

TABLE 15.8 Typical properties of PA 2200 [34].

Properties	Value	Standard
Average grain size	56 μm	ISO 13320-1 Laser diffraction
Bulk density	0.45 g/cm^3	EN ISO 60
Density of laser-sintered part	0.93 g/cm^3	EOS method
Tensile modulus	1700 MPa	EN ISO 527
Tensile strength	48 MPa	EN ISO 527
Elongation at break	24%	EN ISO 527
Flexural modulus	1500 MPa	EN ISO 178
Flexural strength	58 MPa	EN ISO 178
Charpy—Impact strength	53 kJ/m^2	EN ISO 179
Charpy—Notched impact strength	4.8 kJ/m^2	EN ISO 179
Izod—Impact strength	32.8 kJ/m^2	EN ISO 180
Izod—Notched impact strength	4.4 kJ/m^2	EN ISO 180
Ball indentation hardness	78 N/mm^2	EN ISO 2039
Hardness, Shore D	75	ISO 868
Melting point	172–180°C	EN ISO 11357-1

TABLE 15.9 Typical properties of PA 3D HR PA 12 [11].

Properties	Value	Standard
Density of laser-sintered part	1.01 g/cm^3	ASTM D792
Tensile modulus	1900 MPa	D638
Tensile strength	50 MPa	D638
Elongation at break (XY)	17%	D638
Elongation at break (Z)	9%	D638
Impact strength (XY)	4.2 kJ/m^2	ASTM D792
Impact strength (Z)	4.2 kJ/m^2	ASTM D792

TABLE 15.10 Typical properties of PA 3200 GF – polyamide 12 filled with glass beads polymers [34].

Properties	Value	Standard
Average grain size	57 μm	ISO 13320-1 Laser diffraction
Bulk density	$0.63\ \text{g/cm}^3$	EN ISO 60
Density of laser-sintered part	$1.22\ \text{g/cm}^3$	EOS method
Tensile modulus	3200 MPa	EN ISO 527
Tensile strength	51 MPa	EN ISO 527
Elongation at break	9%	EN ISO 527
Flexural modulus	2900 MPa	EN ISO 178
Flexural strength	73 MPa	EN ISO 178
Charpy—Impact strength	$35\ \text{kJ/m}^2$	EN ISO 179
Charpy—Notched impact strength	$5.5\ \text{kJ/m}^2$	EN ISO 179
Izod—Impact strength	$21.3\ \text{kJ/m}^2$	EN ISO 180
Izod—Notched impact strength	$4.2\ \text{kJ/m}^2$	EN ISO 180
Ball indentation hardness	$98\ \text{N/mm}^2$	EN ISO 2039
Hardness, Shore D	80	ISO 868
Melting point	172–180°C	EN ISO 11357-1
Heat deflection temperature	350°F	ASTM D648
Vicat softening temperature B/50	166°C	EN ISO 306
Vicat softening temperature A/50	179°C	EN ISO 306

properties of the models produced and increases the isotropic properties of the material, which in the case of SLS and other 3D printing methods largely depend on the direction of the layers: printing direction. Table 15.10 shows selected properties of the PA 3200 GF polyamide. This material is a powder with a grain diameter of 57 μm, which allows for the production of models with a layer thickness of less than 0.1 mm. In the case of the PA 3200 GF polyamide, we are dealing with a polyamide based on Polyamide PA 2200 (PA 12) enriched with GF, which increases the durability of the models produced compared to those obtained with the use of pure PA 12 (PA 2200). Young's modulus is more than twice that of pure PA 2200 (PA 12). When analyzing the density of both the sintered material and the powdered plastic, it can be seen that this material is over 30% heavier than pure polyamide. Although the tensile strength remains at a similar level (6% differences), polyamide reinforced with GF is characterized by a much lower elongation at break, as well as a lower strength determined during dynamic tests (Charpy test). Hardness of pure PA 12 (PA 2200) as enriched with carbon fiber remains at a similar level of 75 and 80 (Shore D), respectively. This material is perfect for the construction of elements from which we expect very high stiffness and abrasion resistance, such as housings, covers, elastic elements such as bellows, etc. Moreover, as the research shows, models made of this material are characterized by high-dimensional and shape stability and small deviations in shape such as flatness, straightness, cylindricity, and roundness.

15.2.5 Polyamide PA 12 filled with aluminum powder

Another material that is perfect for building models with laser 3D printing technologies, from which we expect increased mechanical properties and high stiffness, is a polyamide powder enriched with aluminum with the trade name Alumide. This material contains a PA 12 polyamide powder additionally mixed with 30% aluminum powder. This material with a grain diameter of 60 μm is based on a well-known construction material and also allows the construction of models with a layer thickness of 0.1 mm. An additional advantage of this polyamide is the fact that ready models can be subjected to finishing treatment, such as grinding, polishing, or coating. In addition, the addition of aluminum has a positive effect on the machining of the manufactured models (chip-breaking effect of the aluminum). The great advantage of this powder is the high thermal resistance of the models produced (Vicat softening temperature B/50 = 169°C). Compared to GF-reinforced polyamide, Alumide has a similar density with a much higher Young's modulus (3200 MPa = PA 3200 GF and 3800 MPa = Alumide). Moreover, impact tests have also shown that the material treated with aluminum is much more resistant to dynamic loads. Both materials are characterized by a similar density value, which for Alumide is 1.36 g/cm^3 and is 11% higher than that of GF-enriched polyamide and 46% higher than pure polyamide based on PA 12. As shown by research works [35] for this material the direction of printing has a very large impact on the density of the sintered model, which is a key factor affecting the weight of the models produced. It is interesting that both the addition of GF and aluminum did not affect the melting point in any way, which for the mentioned powders is 178−180°C.

The Alumide material works very well in the production of machine parts in the automotive industry and in the production of tools in conventional manufacturing technologies such as: tool inserts for injection and molding. The color of the material is similar to pure metal, which allows you to make all kinds of models imitating metal. Due to its stiffness, this material is successfully used to build models in the automotive and aviation industries, which are tested in wind tunnels. Due to the fact that the weight-to-strength ratio in the case of aluminum reinforced polyamide is extremely favorable, the models produced by these powders perfectly fit into the realities of the industrial revolution 4.0 and the concept of LEAN manufacturing, allowing to a large extent optimization of the structure in terms of weight and savings of the material used on the scale of the prototype construction and further mass production using conventional technologies. Table 15.11 presents selected properties of the material in question.

TABLE 15.11 Typical properties of alumide − polyamide 12 filled with aluminum powder [36].

Properties	Value	Standard
Average grain size	60 μm	ISO 13320-1 Laser diffraction
Bulk density	0.67 g/cm^3	EN ISO 61
Density of laser-sintered part	1.36 g/cm^3	EOS method
Tensile modulus	3800 MPa	EN ISO 527
Tensile strength	48 MPa	EN ISO 527
Elongation at break	4%	EN ISO 527
Flexural modulus	3600 MPa	EN ISO 178
Flexural strength	72 MPa	EN ISO 178
Charpy—Impact strength	29 kJ/m^2	EN ISO 179
Charpy—Notched impact strength	4.6 kJ/m^2	EN ISO 179
Hardness, Shore D	76	ISO 868
Melting point	172−180°C	EN ISO 11357-1
Heat deflection temperature	351°F	ASTM D648
Vicat softening temperature B/50	169°C	EN ISO 306
Heat conductivity (170°C)	0.5−0.8 W(mK)-1	Hot wire method
Surface resistance [10 V]	3 × 1012 Ω	IEC 93
Specific surface resistance	5 × 1015 Ω	IEC 93
Volume resistance [10 V]	6 × 1012 Ω	IEC 93
Specific volume resistance	3 × 1014 Ω × cm	IEC 93
Dielectric breakdown strength	0.1 kV/mm	EN 60243-1
Dielectric constant (1 kHz)	13 ± 1.5 (100 Hz)	DIN 53483
Dielectric loss factor (1 kHz)	0.018 ± 0.002	DIN 53483

15.2.6 *Polyamide PA 12 filled with glass beads and carbon fibers*

Polyamide PA 640-GSL from EOS is a material based on polyamide PA 12; however, it is additionally reinforced with the addition of both hollow glass beads and carbon fiber. This makes it exceptionally temperature resistant and rigid, but also very light. This material can be compared with the pure PA 2200 material as well as its counterparts reinforced with GF (PA 3200 GF). The density of the material in the sintered state (ready model) is slightly lower than that of pure polyamide and amounts to 0.82 g/cm^3 (0.93 g/cm^3 = pure PA 2200, 1.22 g/cm^3 = PA 3200 GF). The mechanical properties shown in Table 15.12 also resemble pure PA 2200 polyamide than the previously discussed Alumide and PA 3200 GF. It is interesting that despite the lower mass, it was possible to obtain a similar value of the Young's modulus amounting to 1945 MPa, the value of which, while maintaining the smaller mass of the produced models, is much higher than for pure polyamide (1700 MPa). Another key strength parameter which, despite having a weight lower by 12% than that of pure polyamide, shows higher values is tensile strength. The tensile strength value for polyamide PA 640-GSL is 49 MPA, 1 MPa more than PA 2200. It would seem that this material has only advantages; however, despite higher strength compared to pure polyamide, this material is characterized by a very low value elongation at break, which in this case is only 3% and is more like Alumide material (Elongation at Break = 4%), pure PA 2200 is characterized by an elongation at break of 24%. The large elongation is of great justification in the construction of machine elements that work under load; hence it can be assumed that in such applications PA 2200 will be a better choice.

15.2.7 *Polyamide PA 12 flame-retardant (PrimePart FR)*

The polyamide with the trade name PrimePart FR is a powder based on PA 12 polyamide, which has been additionally enriched with halogen flame retardant (reducing its flammability). Due to the high market demand, especially in the case of short production series, this material is a response to the growing demand of the aviation, morotization, and medical industries. This material meets the fire resistance class standards: CS 25/JAR25/FAR 25 § 25-853 (a) App. F Part I, ABD 0031. Meeting these rigorous standards means that this material can be used to build not only prototypes but also fully functional models. This material has a very high recovery rate, which means that it can be recycled in the case of material that has not undergone the sintering process. The recovery of unused powder, which played the role of either a supporting material or filling the chamber during construction, is a key economic factor when choosing a given 3D printing technology and a specific material. In many cases, the recovery is only 30% of the new mixture, which means that the powder must be made up to 70% with new material and then screened and mixed before reuse. Compared to pure PA 2200 (PA 12), this material shows both slightly higher tensile modulus and tensile strength. Moreover, the material density of 1 g/cm^3 is higher than that of pure polyamide (0.93 g/cm^3). However, when analyzing the density of the material in the so-called of the powder, it can be said

TABLE 15.12 Typical properties of PA 640-GSL—polyamide 12 filled with glass beads and carbon fibers [36].

Properties	Value	Standard
Average particle size (D50)	55 μm	Laser diffraction
Bulk density	0.37 g/cm^3	ASTM D1895
Sintered part density	0.82 g/cm^3	ASTM D792
Tensile modulus (XY)	3816 MPa	ASTM D638
Tensile modulus (Z)	1945 MPa	ASTM D638
Tensile strength (XY)	49 MPa	EN ISO 527
Tensile strength (Z)	33 MPa	EN ISO 527
Elongation at Break	3%	ASTM D638
Flexural modulus (XY)	5040 MPa	ASTM D790
Flexural modulus (Z)	4313 MPa	ASTM D790
Heat detection temperature	170°C	ASTM D648

that it is the same in both cases (0.45 g/cm^3). A similar situation applies to the previously analyzed material (PA 640-GSL), where also the material in the powder state showed a very low density value, but in the sintered state it was more than twice as high as the density of the powder itself. Selected material properties are shown in Table 15.13.

15.2.8 Polyamide PA 11

Polyamide PA 11 is a material similar to pure polyamide PA 12. In the case of the SLS technology and the technology offered by EOS GmbH, we have four types of PA 11 polyamide blends: pure PA 11 polyamide with the trade name PA 1101 white and PA 1101 black; HP 11-30—Polyamide 11 Filled With Carbon Fibers; and FR-106—Flame-Retardant. In the case of pure polyamide PA 1101 White and 1102 Black, the material density is 0.99 g/cm^3. Analyzing the strength-to-weight ratio of the manufactured models, it can be said that the materials based on polyamide PA 11 show a slightly worse ratio.

Pure PA 11 polyamide with the trade name PA 1101 White from EOS, with the properties presented in Table 15.14, has a slightly lower toughness compared to polyamide PA 12. It is particularly visible in the case of tensile modulus, where in the case of pure PA 2200 based on PA 12, the strength is 100 MPa higher than the PA 11 shown. Tensile strength and Shore hardness are very similar. However, the elongation at break parameter is interesting, as it amounts to as much as 45%, which is a very high value compared to pure PA 2200 polyamide, for which the average value is 24%.

Another example of a powdered material based on PA 11 polyamide is the material with the trade name PA 1101 Black with the properties shown in Table 15.15. When analyzing the values in Tables 15.14 and 15.15 for PA 1101

TABLE 15.13 Typical properties of PrimePart FR (PA 2241 FR)—polyamide 12 flame-retardant [36].

Properties	Value	Standard
Bulk density	0.45 g/cm^3	EN ISO 60
Sintered part density	1 g/cm^3	ASTM D792
Tensile modulus	1900 MPa	EN ISO 527
Tensile strength (X)	49 MPa	EN ISO 527
Tensile strength (Y)	49 MPa	EN ISO 527
Tensile strength (Z)	46 MPa	EN ISO 527
Melting temperature (20°C/min)	185 °C	ASTM D648
Heat deflection temperature (1.80 MPa)	84°C	ASTM D648
Strain at break (X)	15%	EN ISO 527
Strain at break (Y)	15%	EN ISO 527
Strain at break (Z)	6%	EN ISO 527

TABLE 15.14 Typical properties of Polyamide 11—PA 1101 white [36].

Properties	Value	Standard
Tensile modulus	1600 MPa	EN ISO 527
Tensile strength	48 MPa	EN ISO 527
Elongation at Break	45%	EN ISO 527
Charpy—Notched impact strength	7.8 kJ/m^2	EN ISO 179
Hardness, Shore D	75	ISO 868
Sintered part density	0.99 g/cm^3	EOS method

TABLE 15.15 Typical properties of Polyamide 11—PA 1102 black [36].

Properties	Value	Standard
Tensile modulus	1560–1610 MPa	EN ISO 527
Tensile strength	28–48 MPa	EN ISO 527
Elongation at Break	45%	EN ISO 527
Charpy—Notched impact strength	7.8 kJ/m^2	EN ISO 179
Hardness, Shore D	75	ISO 868
Sintered part density	0.99 g/cm^3	EOS method

TABLE 15.16 Typical properties of HP 11-30—Polyamide 11 filled with carbon fibers [37].

Properties	Value	Standard
Tensile modulus (XY)	3300 MPa	ASTM D638
Tensile modulus (Z)	2600 MPa	ASTM D638
Tensile strength (XY)	56 MPa	ASTM D638
Tensile strength (Z)	46 MPa	ASTM D638
Elongation at Break	8%–9%	ASTM D638
Sintered part density	0.99 g/cm^3	EOS method
Average particle size (D50)	80 μm	Laser diffraction

White and PA 1102 Black, it can be said that they show almost identical properties, and the only difference is their appearance in the form of colors.

15.2.9 Polyamide PA 11 filled with carbon fibers

Another example of a modified material based on polyamide PA 11 is HP 11-30—Polyamide 11 Filled With Carbon Fibers. This material, as shown in Table 15.16, is characterized by much better strength properties while maintaining a very good weight-to-strength ratio. This material is reinforced with carbon fiber, which, as can be seen, significantly increases the strength. The tensile modulus increases very clearly from 1600 MPa (PA 1101 and PA 1102) to 2600–3300 MPa. Moreover, the tensile strength expressed by the tensile strength parameter increases from 48 to 56 MPa for the selected printing directions (XY).

15.2.10 Polyamide PA 11 flame-retardant

Another example of a modified material based on polyamide PA 11 is FR-106—Polyamide 11 Flame-Retardant. This material, as shown by the data presented in Table 15.17, has strength properties similar to those of pure polyamide PA 11. This mainly applies to tensile strength and tensile modulus. When analyzing the density value of the material in the sintered state, it can be said that the FR-106 material is the heaviest of the mentioned PA 11 polyamides. Comparing this material with pure PA 12 (PA 2200), it can be said that its density is also higher. Compared to the PA 12 Flame-Retardant polyamide, the PA 11 FR polyamide also has a higher density. As can be seen, the introduction of an additive increasing the flame resistance reduces the tensile strength while increasing the weight of the models produced.

15.2.11 Polyamide PA 6

Polyamide rarely used in commercial 3D printing systems as a powder is polyamide based on polyamide PA 6. Tables 15.18 and 15.19 provide information on the material based on polyamide PA 6 with the trade name Ultrasint PA6 FR and PA6 MF X036.

TABLE 15.17 Typical properties of FR-106—Polyamide 11 flame-retardant [38].

Properties	Value	Standard
Tensile modulus (XY)	1392 MPa	ASTM D638
Elongation at break (Z)	38%	ASTM D638
Sintered part density	1.07 g/cm^3	EOS method
Build density	0.45 g/cm^3	ASTM D1895
Average particle size (D50)	95 μm	Laser diffraction

TABLE 15.18 Typical properties of Ultrasint® PA6 FR [39].

Properties	Value	Standard
Tensile modulus	2500 MPa	ASTM D638
Tensile strength	41 MPa	ASTM D638
Elongation at break (Z)	3%	ASTM D638

TABLE 15.19 Typical properties of PA6 MF X036 [40].

Properties	Value	Standard
Tensile modulus	5850—6400 MPa	ISO 527-2
Tensile strength	74—86 MPa	ISO 527-2
Elongation at break (Z)	1.7%—2.5%	ASTM D638
Sintered part density	1.44 g/cm^3	ISO 1183-1
Build density	0.63 g/cm^3	ISO 696
Average particle size (D50)	72 μm	Laser diffraction

15.3 Polyetherketoneketone reinforced with carbon fibers

The analyzed material, under the trade name HT-23, is from the group of polyetherketoneketones (PEKKs). PEKK materials are semicrystalline aromatic polyesters with excellent mechanical and dielectric properties. In addition, they are fire retardant with good chemical resistance. The material is approved for parts destined for the interior of trains (DIN EN 45545-2: 2016 standard), Requirement Sets R1 and R24. The advantage of the presented material compared to other known PEKK materials is the addition of 23% carbon fibers encapsulated (compounded) in the round powder grains of the material. The advantage of the presented material is a very high degree of isotropic mechanical properties, which is typical for the enrichment of materials with additives in the form of GFs (polyamide PA 3200 GF). Comparing this material with the previously described polyamides (PA 2200, PA 3200 GF), it can be noticed that HT-23 is characterized by a much higher strength expressed both by this modulus strength (5.8—6.5 GPa) and tensile strength (61—80 MPa). This material is characterized by a very low elongation at break amounting to 1%, which is a very small value compared to pure polyamide (24%). Table 15.20 presents selected properties of the material in question. In addition, Chapter 14, Section 14.4.2, presents selected properties of the PEKK material used in the FDM/FFF technology, however, delivered to the printer in the form of a solid filament. Comparing the properties of both materials, it can be said that PEKK powder (1.39 g/cm^3) has a slightly higher density compared to PEKK in the form of a filament (1.28—1.31 g/cm^3). Differences are also visible in the strength of the models produced, where the tensile strength of the powder is 61—80 MPa, and of the filament 90—110 MPa.

TABLE 15.20 Typical properties of HT-23 polyetherketoneketone reinforced with carbon fibers [36].

Properties	Value	Standard
Average particle size (D50)	80 μm	Laser diffraction
Bulk density	0.5 g/cm^3	ASTM D1895
Density of laser-sintered part	1.39 g/cm^3	ASTM D792
Tensile modulus (X)	6.5 GPa	ASTM D638
Tensile modulus (Y)	6.4 Gpa	ASTM D638
Tensile modulus (Z)	5.8 Gpa	ASTM D638
Tensile strength (X)	80 Mpa	ASTM D638
Tensile strength (Y)	77 Mpa	ASTM D638
Tensile strength (Z)	61 Mpa	ASTM D638
Elongation at break	1.16% XY/1.06% ZX	ASTM D638
Strain at break (X)	1.3%	ASTM D638
Strain at break (Y)	1.3%	ASTM D638
Strain at break (Z)	1.1%	ASTM D638
Flexural modulus	5.97 GPa/5.13 GPa	ASTM D790
Flexural strength	101 MPa/81 MPa	ASTM D790
IZOD impact strength (unnotched)	80 J/m/101 J/m	ASTM D256
IZOD impact strength (notched)	20 J/m/18 J/m	ASTM D256
Melting point	302 °C	ASTM D3418
Heat deflection temp (0.45 MPa)	375°F	ASTM D648

15.4 Thermoplastic elastomer

Powder materials used in 3D printing technologies usually show very high tensile and compressive strength and are characterized by a large Young's modulus. However, in many applications, additive manufacturing models are expected to be highly flexible and have properties similar to those of the Rubber group. TPU (EOS) material is one such powder. It allows the production of models with a very high flexibility and a wide practical range of applications. These models include, for example, the very popular flexible bellows and snap connections as well as many types of flexible covers and housings. The bellows can serve as a sealing as well as dampen vibrations and perform the role of pneumatic muscles in the robotics industry. In the era of industry 4.0, it is a very desirable material with which you can compare few other materials used in other 3D printing technologies. The parts made from this white material are extremely hydrolysis-resistant, with high resilience and good tribological properties. Comparing this material with HT-23 from the PEKK group and the described polyamides, it can be seen that the powder itself is similar in density to HT-23, but its properties are completely different. The biggest difference is the huge value of elongation at break, which is between 90% and 250%. As you can see, it is one of the few, if not the only, material in the SLS technology or HP Jet Fusion technology at present to show such a high elongation at break value. In the case of 3D printing technology, this material can be compared with Tango Black, which is used in the photocurable technology of liquid polymer resins—PJM. Undoubtedly, this material is suitable for the construction of models that are required to work continuously in terms of stresses that cause its large deformations, without damaging the model during operation and, as already mentioned, it is perfectly suited for the construction of both elastic bellows and all kinds of manipulators and elements in robotics industry, where 3D printing is experiencing a great development. Table 15.21 presents selected properties of TPU 1301 material. Selected properties of TPU material in the form of filament are presented in Chapter 14, Section 14.3.6.

TABLE 15.21 Typical properties of EOS TPU 1301 [36].

Properties	Value	Standard
Average particle size (D50)	72 μm	Laser diffraction
Bulk density	0.49 g/cm^3	EN ISO 60
Density of laser-sintered part	1.11 g/cm^3	EN ISO 1183-1
Tensile modulus	50–60 MPa	EN ISO 527
Tensile strength X/Y	7 MPa	EN ISO 527
Tensile strength Z	5 MPa	EN ISO 527
Elongation at break X/Y	250%	EN ISO 527
Elongation at break Z	90%	EN ISO 527
Melting point	138°C	DIN 53736

TABLE 15.22 Typical properties of PEBA [41].

Properties	Value
Density of laser-sintered part	1–1.03 g/cm^3
Tensile strength at break	32–56 MPa
Elongation at break	300%–750%
Melting point	134–174°C
Shore hardness	25–72

Another example from the TPU group is a material called PEBA, which appears under several names: PEBAX® (Arkema) and VESTAMID® E (Evonik Industries). It is a block copolymer obtained by polycondensation of a carboxylic acid polyamide with an alcohol termination polyether. Example properties of PEBA material are presented in Table 15.22. Comparing the properties of the PEBA material with the previously described TPU 1301, it can be said that it shows above all a much greater elongation at break, which reaches even 750% compared to 250% for TPU.

15.5 Polystyrene

Another powder material used in laser 3D printing of plastics is PrimeCast 101 from EOS. This material belongs to the group of thermoplastic materials and has a powder grain diameter of 80 μm. Such a large size of grains means that models made of this material must be manufactured with a given layer thickness of 0.15 mm, which is a large value compared to models made of, for example, PA 2200 or PA 3200 GF and Alumide polyamide. The density of the material in the sintered state, i.e., for the finished model, is low compared to the previously discussed materials and amounts to 0.7–0.85 g/cm^3. According to the manufacturer, this material is intended mainly for the production of models for the investment casting industry, due to its excellent dimensional accuracy and its low melting point. It can be said that it is the foundry that is the main, if not the only recipient of this material, which results from its low strength properties, while maintaining a very high dimensional stability. Table 15.23 presents selected properties of the material in question. In Chapter 14, Section 14.2.3, one can find and compare information on the same material, however, supplied in the form of a solid for FDM/FFF technology.

TABLE 15.23 Typical properties of PrimeCast® 101 — polystyrene [36].

Properties	Value	Standard
Average particle size	80 μm	Coulter counter
Bulk density	0.61 g/cm^3	DIN 53466
Density of laser-sintered part	0.7–0.85 g/cm^3	EOS method
Tensile modulus	1600 MPa	EN ISO 527
Tensile strength (XY)	5.5 MPa	EN ISO 527
Tensile strength (Z)	1.2 MPa	EN ISO 527
Elongation at break	0.4%	EN ISO 527
Glass transition temperature	105°C	DIN 53765
Material destruction	250–550°C	DIN 51006
Remaining ash content	0.002	EOS method

TABLE 15.24 Typical properties of PP 1101 — polypropylene [36].

Properties	Value	Standard
Density of laser-sintered part	0.9 g/cm^3	EOS method
Tensile modulus	1200 MPa	EN ISO 527
Tensile strength	27 MPa	EN ISO 527
Strain at break	12%	EN ISO 527
Izod impact strength (+23°C)	3 kJ/m^2	EN ISO 180

15.6 Polypropylene

PP 1101 polypropylene powder is a material with relatively low strength properties, where tensile modulus is 1200 MPa, a tensile strength 27 MPa. Table 15.24 presents selected properties of the material in question. Despite its low strength properties, this material has excellent resistance to chemicals, especially sulfuric acid, formic acid, potassium permanganate, hydrochloric acid, sodium hydroxide solution, fuels, and alcohols. An important factor is also a very low water absorption, which allows the use of finished models in an environment with high humidity. Such conditions are conducive to the use of this material for the construction of prototype models, in particular to carry out real tests, simulate flows of all types of liquids and gases, also with a high degree of contamination. In addition, the production of laboratory equipment that requires high chemical resistance is a large potential market for polypropylene. The medical and cosmetic industries also appreciate the presented properties, as very often manufactured models are intended to serve mainly as containers for storage and transport, where high strength is not a key factor, but chemical resistance. Chapter 14, Section 14.2.1 presents selected properties of the PP equivalent, however, used in technologies based on solid material.

15.7 Polyphenylene sulfide

Polyphenylene sulfide powder is a plastic, in powder form, that is used in the Powder Bed Fusion (PBF) process, which is one of the major 3D printing process. The powder with the trade name Toraymill™ PPS with the properties presented in Table 15.25 is a material with very good strength properties, in particular high fatigue resistance. This material exhibits good electrical characteristics and dimensional stability and excellent long-term heat resistance. The low cost of building models using this powder and the possibility of further machining make this material an alternative to various types of polyamides. This material is also available in variants where it is reinforced

TABLE 15.25 Typical properties of polyphenylene sulfide [42].

Properties	Value
Tensile strength	49 MPa
Tensile elongation	2.2%
Melting point	280°C

with GF fiber and CF carbon fiber. In these variants, it takes the following parameters: Tensile strength (GF = 65 and CF = 87), Tensile elongation (GF = 2.3 and CF = 1.0).

15.8 Conclusions

Summarizing the presented chapter on polymer powders used in additive manufacturing technologies, it can be stated that over the last few decades there has been a huge development in the chemistry of materials/powders, which results in an increase in the number of new 3D printing materials available on the market. As mentioned above, these properties are so satisfactory that we have both materials with a high degree of stiffness and very flexible materials with their properties resembling rubber. Polymers, the production of which has been known for years, as well as the production of powder, are an excellent building material that does not require the use of support structures that are difficult to remove. Moreover, the simplicity of introducing additives in the form of carbon, glass, or aluminum fibers, as shown above, or flame-retardant additives make the production of new materials very simple.

The key in the case of powder-based 3D printing technology, as shown by the research results, is the selection of appropriate technological parameters, which affect both the strength, dimensional accuracy and tribological wear of the models produced, as well as the correct powder sintering process. In the era of high development of 3D printing and the increasing popularity of laser technologies based on polymer powders, it can be said that these technologies and materials will experience enormous development in the next few decades, greater commercialization of new cheap machines and materials.

References

[1] T. Kozior, The influence of selected selective laser sintering technology process parameters on stress relaxation, mass of models, and their surface texture quality, 3D Print. Addit. Manuf. 7 (3) (2020) 126–138, https://doi.org/10.1089/3dp.2019.0036.

[2] C.R. Deckard, R. Rock, J. Joseph, Method for Selective Laser Sintering with Layerwise Cross-Scanning, 1992, p. 12. https://patents.google.com/patent/US5155324A/de15.

[3] T.D. Ngo, A. Kashani, G. Imbalzano, K.T.Q. Nguyen, D. Hui, Additive manufacturing (3D printing): a review of materials, methods, applications and challenges, Compos. B Eng. 143 (2018), https://doi.org/10.1016/j.compositesb.2018.02.012.

[4] C.K. Chua, K.F. Leong, 3D Printing and Additive Manufacturing, 2014, https://doi.org/10.1142/9008.

[5] C.K. Chua, K.F. Leong, 3D Printing and Additive Manufacturing: Principles and Applications: The 5th Edition of Rapid Prototyping: Principles and Applications, 2017, https://doi.org/10.1142/10200.

[6] N. Guo, M.C. Leu, Additive manufacturing: technology, applications and research needs, Front. Mech. Eng. 8 (2013), https://doi.org/10.1007/s11465-013-0248-8.

[7] T. Kozior, J. Bochnia, The influence of printing orientation on surface texture parameters in powder bed fusion technology with 316L steel, Micromachines 11 (2020), https://doi.org/10.3390/MI11070639.

[8] C. Kundera, T. Kozior, The Influence of Selective Laser Sintering Parameters on Tribological Properties of PA 3200 GF Polyamide, Tribologia, 2018, https://doi.org/10.5604/01.3001.0011.9856.

[9] T. Kozior, Analysis of the Influence of Process Parameters of Selected Additive Technologies on the Geometry and Mechanical Properties of Products, Kielce University of Technology, 2018.

[10] M. Baumgarten, The Chemistry of Polymers. (Reihe: Royal Society of Chemistry, Paperbacks.) Von J. W. Nicholson, The Royal Society of Chemistry, London, 1991–1992, https://doi.org/10.1002/ange.19921040345. XII. 174 S., Broschur £ 14.50. — ISBN 0-85186-413-9, Angew. Chemie.

[11] HP Jet Fusion, HP 3D Printing materials for the HP Jet Fusion 5200 Series 3D Printing Solution. Mechanical Properties, 2020. https://h20195.www2.hp.com/V2/getpdf.aspx/4AA7-7084ENW.pdf (Accessed 20 January 2020).

[12] C. Kundera, T. Kozior, Elastic bellows prepared by selective laser sintering, Appl. Mech. Mater. 630 (2014), https://doi.org/10.4028/www.scientific.net/AMM.630.318.

[13] C. Kundera, T. Kozior, Research of the elastic properties of bellows made in SLS technology, Adv. Mater. Res. 874 (2014), https://doi.org/10.4028/www.scientific.net/AMR.874.77.

[14] C. Kundera, T. Kozior, Evaluation of the influence of selected parameters of Selective Laser Sintering technology on surface topography, J. Phys. Conf. Ser. 1183 (2019), https://doi.org/10.1088/1742-6596/1183/1/012002.

[15] T. Kozior, Rheological properties of polyamide pa 2200 in SLS technology, Teh. Vjesn. 4 (2020), https://doi.org/10.17559/TV-20190225122204.

[16] J. Bochnia, T. Kozior, Methods of prototyping process using modern additive technologies, Solid State Phenom. 223 (2015), https://doi.org/10.4028/www.scientific.net/SSP.223.199.

[17] A. Pilipovic, B. Valentan, T. Brajlih, T. Haramina, J. Balic, J. Kodvanj, M. Sercer, I. Drstvensek, Influence of laser sintering parameters on mechanical properties of polymer products, in: Annals of DAAAM and Proceedings of the International DAAAM Symposium, 2010.

[18] C.S.M. Borzan, M.C. Dudescu, V. Ceclan, A. Trif, M. Ridzon, P. Berce, PA 2200 vs. PMMA: comparison between the mechanical proprieties obtained for the 2 biocompatible materials, Mater. Plast. 53 (2016).

[19] C.S. Miron-Borzan, M.C. Dudescu, P. Berce, Bending and compression tests for PA 2200 parts obtained using Selective Laser Sintering method, in: MATEC Web Conference, 2017, https://doi.org/10.1051/matecconf/20179403010.

[20] C. Borzan, P. Berce, H. Chezan, E. Sabəu, S.A. Radu, M. Ridzon, Physico-mechanical properties characterization of the parts from PA 2200 manufactured by Selective Laser Sintering technology, Acad. J. Manuf. Eng. 11 (2013).

[21] A. Wegner, New polymer materials for the laser sintering process: polypropylene and others, Phys. Procedia 83 (2016), https://doi.org/10.1016/j.phpro.2016.08.105.

[22] C.S.M. Borzan, M. Moldovan, V. Bocanet, Evaluation of surface modification of PA 2200 parts made by selective laser sintering process, Rev. Chim. (Bucharest) 69 (2018), https://doi.org/10.37358/rc.18.4.6221.

[23] T. Blachowicz, A. Ehrmann, 3D printed MEMS technology-recent developments and applications, Micromachines 11 (2020), https://doi.org/10.3390/MI11040434.

[24] G.V. Salmoria, P. Klauss, L.A. Kanis, Laser printing of PCL/progesterone tablets for drug delivery applications in hormone cancer therapy, Lasers Manuf. Mater. Process 4 (2017), https://doi.org/10.1007/s40516-017-0040-4.

[25] G.V. Salmoria, F.E. Vieira, E.A. Muenz, I.M. Gindri, M.S. Marques, L.A. Kanis, Additive Manufacturing of PE/fluorouracil/progesterone intrauterine device for endometrial and ovarian cancer treatments, Polym. Test. 71 (2018), https://doi.org/10.1016/j.polymertesting.2018.09.023.

[26] G.V. Salmoria, F.E. Vieira, G.B. Ghizoni, M.S. Marques, L.A. Kanis, 3D printing of PCL/Fluorouracil tablets by selective laser sintering: properties of implantable drug delivery for cartilage cancer treatment, Rheumatol. Orthop. Med. 4 (6) (2017), https://doi.org/10.15761/rom.1000121.

[27] G.V. Salmoria, R.A. Paggi, A. Lago, V.E. Beal, Microstructural and mechanical characterization of PA12/MWCNTs nanocomposite manufactured by selective laser sintering, Polym. Test. 30 (2011), https://doi.org/10.1016/j.polymertesting.2011.04.007.

[28] G.V. Salmoria, J.L. Leite, R.A. Paggi, The microstructural characterization of PA6/PA12 blend specimens fabricated by selective laser sintering, Polym. Test. 28 (2009), https://doi.org/10.1016/j.polymertesting.2009.06.010.

[29] G.V. Salmoria, J.L. Leite, L.F. Vieira, A.T.N. Pires, C.R.M. Roesler, Mechanical properties of PA6/PA12 blend specimens prepared by selective laser sintering, Polym. Test. 31 (2012), https://doi.org/10.1016/j.polymertesting.2011.12.006.

[30] G.V. Salmoria, J.L. Leite, R.A. Paggi, A. Lago, A.T.N. Pires, Selective laser sintering of PA12/HDPE blends: effect of components on elastic/plastic behavior, Polym. Test. 27 (2008), https://doi.org/10.1016/j.polymertesting.2008.04.007.

[31] G.V. Salmoria, E.A. Fancello, C.R.M. Roesler, F. Dabbas, Functional graded scaffold of HDPE/HA prepared by selective laser sintering: microstructure and mechanical properties, Int. J. Adv. Manuf. Technol. 65 (2013), https://doi.org/10.1007/s00170-012-4277-y.

[32] J. Bochnia, S. Blasiak, Fractional relaxation model of materials obtained with selective laser sintering technology, Rapid Prototyp. J. 25 (2019), https://doi.org/10.1108/RPJ-11-2017-0236.

[33] M. Vesenjak, L. Krstulović-Opara, Z. Ren, Characterization of photopolymer cellular structure with silicone pore filler, Polym. Test. 31 (2012), https://doi.org/10.1016/j.polymertesting.2012.04.007.

[34] EOS GmbH, Plastic 3D Printing, 2020. https://www.eos.info/en/additive-manufacturing/3d-printing-plastic (Accessed 20 January 2020).

[35] D.I. Stoia, L. Marsavina, E. Linul, Mode I fracture toughness of polyamide and alumide samples obtained by selective laser sintering additive process, Polymers 12 (2020), https://doi.org/10.3390/polym12030640.

[36] EOS GmbH, Additive Manufacturing solutions & industrial 3D printer by EOS, 2020. https://www.eos.info/en (Accessed 20 January 2020).

[37] Advanced Laser Materials, Laser Sintering Specification, 2020. https://alm-llc.com/wp-content/uploads/2019/04/HP-11-30.pdf (Accessed 20 January 2020).

[38] Advanced Laser Materials, FR-106, 2020. https://alm-llc.com/wp-content/uploads/2019/04/FR-106.pdf (Accessed 20 January 2020).

[39] BASF 3D Printing Solutions GmbH, PA 6, 2020. https://forward-am.com/find-material/powder-bed-fusion/ultrasint-pa6-2/ultrasint-pa6-fr/ (Accessed 20 January 2020).

[40] BASF 3D Printing Solutions GmbH, Technical Data Sheet. Ultrasint PA6 MF X036, 2018. https://www.fkm.net/wp-content/uploads/2019/02/PA6_MF_X036.pdf (Accessed 20 January 2020).

[41] S. Fakirov, Handbook of Condensation Thermoplastic Elastomers, 2006, https://doi.org/10.1002/3527606610.

[42] TORAY, Polymer milled powder Toraymill™ PPS, 2018. https://www.toray.jp/chemical/en/polymer/pol_004h.html (Accessed 20 January 2020).

CHAPTER

16

Plastic pellets

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16.1 Necessity of pellet-based 3D printing

The material in filament form is necessarily required to fabricate parts using the fused filament fabrication (FFF) process. Only polymers having specific mechanical properties can be processed through the filament feeding mechanism of FFF. Also, various manufacturing steps are involved in the filament preparation with desired size and shape. Moreover, slightly positive or negative variation in diameter might be accountable for slippage or crushing of filament in between the rotating rollers of FFF. Therefore, alternative 3D printing processes are evolved to process other material shapes, i.e., pellets [1,2].

The direct use of pellets for 3D printing could play a vital role which may overcome the issues related to filament printing. It enables direct part fabrication without preparing material in the form of the standard filament. Further, manufacturing steps of filament making can be eliminated with the use of pellets. Also, the chance of material contamination would be minimized with fewer manufacturing steps. Therefore, this could provide more reliable parts at a cheaper rate than that of filament-based 3D printing. Thus, pellet-based extrusion 3D printing systems can be a good alternate to FFF for part printing. With pellet-based systems, those polymer materials can also be investigated in the 3D printing domain which is not explored yet through FFF systems.

16.2 Introduction and classification of polymer pellets

Pellets are small shape polymer granules (spherical or barrel-shaped) that are few millimeters in diameter, which serve as raw material for various plastic manufacturing processes. Common types of pellets used in industries are acrylonitrile butadiene styrene (ABS), polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyvinyl chloride (PVC), polyethylene terephthalate (PET), etc. Polymer pellets are widely used in the plastic industry for making a variety of products of different shapes and sizes. Plastic can be defined as an organic high polymer that changes shape with the application of pressure of force and retains after removal of the force. Nowadays, a variety of synthetic plastics exist which can be classified as:

1. thermoplastic,
2. elastomers,
3. thermosetting.

16.2.1 Thermoplastics

Thermoplastics are chemically independent micromolecular structure, which softens or melts by heating, thus can be reshaped, solidifies when cooled. Thermoplastics can be heated and cooled several times without any severe

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damage in chemical structure or molecular structure and can be recycled or reprocessed several times. Mechanical and rheological properties of thermoplastics can be improved by combining them with additives or fillers.

16.2.1.1 *Semicrystalline*

Most of the common plastics used for day-to-day applications are semicrystalline. These polymers consist of amorphous and crystalline nature. The crystallinity in polymers is in the range of 10%–80% and affects the properties of polymers. 100% crystallinity is never achieved. Semicrystalline polymers have highly ordered molecular structures with precise melting points. With the increase in temperature, the material does not melt gradually; instead it will absorb the heat and will change into a low viscous liquid.

16.2.1.2 *Amorphous*

Amorphous polymers are polymer chains with irregular molecular orientation, which are anisotropic of thermal properties. This polymer can have regular molecular orientation for shorter chains. If the amorphous thermoplastic is heated gradually, it will be converted from a glass state or rigid state to rubber and finally melts. This molten consistency is known as glass transition temperature (T_g). Amorphous thermoplastics are usually transparent in nature as compared to semicrystalline which are opaque. Different semicrystalline and amorphous polymers are listed in Fig. 16.1.

Based on applications and uses thermoplastics can be further categorized into three types, i.e.:

- commodity plastics,
- engineering plastics,
- high-performance plastics.

16.2.1.3 *Commodity plastics*

Commodity plastics are produced in high volumes for daily application uses without outstanding mechanical properties. They have low mechanical properties and are the least expensive. These types of plastics are mostly used for making films for packaging, beverage bottles, trash containers, photo films, etc. Examples of commodity plastics are polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), and polystyrene (PS). Among these, some important commodity plastics are discussed below.

16.2.1.3.1 Polyethylene

Polyethylene is the most commonly and cost-effective plastic used everywhere. PE can be processed easily and can be transformed into varieties of shapes and forms. PE has the ability to alter easily during processing, thus gives relatively longer chain length, density, and crystallinity, allowing PE products to have tailored properties for a variety of applications. High-density polyethylene (HDPE) and low-density polyethylene (LDPE) are some types of PE plastic. HDPE is lightweight and has good tensile strength, whereas LDPE has good chemical resistance. Table 16.1 shows mechanical properties of PE material.

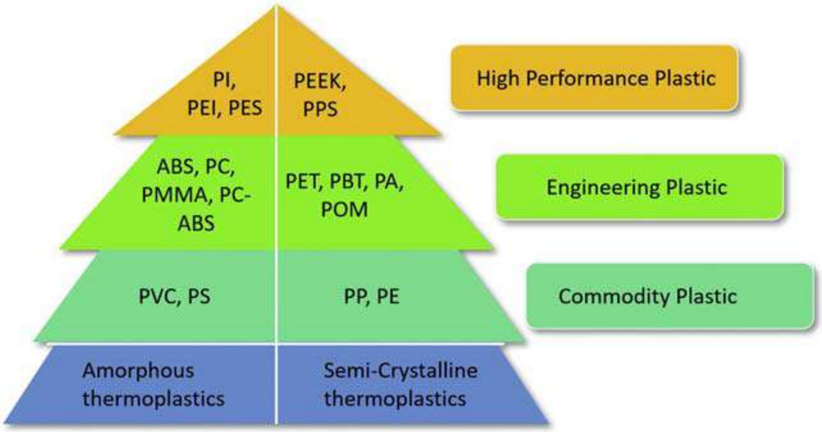

FIGURE 16.1 Thermoplastics available for different applications.

TABLE 16.1 Mechanical properties of polyethylene material.

Property	Typical value
Density (g/cm^3)	0.952–0.965
Tensile strength (MPa)	26.2–31
Strain at break (%)	11–13
Tensile modulus (GPa)	1.07
Printing temperature (°C)	230–260
Melting temperature (°C)	130 ± 10

TABLE 16.2 Mechanical properties of polypropylene material.

Property	Typical value
Density (g/cm^3)	1.04–1.06
Tensile strength (MPa)	31–45
Strain at break (%)	50
Tensile modulus (GPa)	1.5–3
Printing temperature (°C)	230–260
Melting temperature (°C)	160 ± 10

16.2.1.3.2 Polypropylene

Polypropylene is a rigid thermoplastic with semicrystalline in nature with wide everyday applications like packaging tray, household products, medical devices, etc. Properties of PP can be determined by the level of crystallinity, crystalline morphology, and its orientations. PP is among the cheapest plastics available. Mechanical properties of PP are discussed in Table 16.2.

16.2.1.4 Engineering plastics

Engineering plastics are specially designed plastic to withstand high mechanical strength, chemical resistance, and high thermal properties as compared to commodity plastics. Commodity and engineering plastics together serve a wide range of applications such as household applications, industrial components, etc. Examples of engineering plastics are ABS, polycarbonate (PC), polymethyl methacrylate (PMMA), PET, polybutylene terephthalate (PBT), polyamide (PA), polyoxymethylene (POM), etc. Among these, some important commodity plastics are discussed below.

16.2.1.4.1 Acrylonitrile butadiene styrene

Acrylonitrile butadiene styrene is one of the most commonly used engineering plastic that consists of the styrene-acrylonitrile copolymer and butadiene styrene (synthetic rubber) copolymer in glassy matrix form. Optimum properties of ABS can be achieved through appropriate compounding of glassy and rubbery phases. ABS copolymers are relatively tough, have good thermal resistance, and have properties superior than polystyrene plastics. ABS has a wide range of applications such as automotive parts, domestic appliances parts, furniture parts, toys, etc. The mechanical properties of ABS material are listed in Table 16.3.

16.2.1.4.2 Polylactic acid

Polylactic acid (PLA) is a biodegradable material made from renewable organic sources such as corn starch or sugarcane. PLA is available in both bio-based and biodegradable based and is widely used for disposal packaging applications. Compared to traditional synthetic plastics, PLA is expensive and has less mechanical and physical properties. PLA has great biomedical applications such as tissue engineering, cardiovascular implants, drug carriers, orthopedic implants, etc. PLA is one of the most commonly used materials for 3D printing. Table 16.4 shows the mechanical properties of PLA material.

TABLE 16.3 Mechanical properties of ABS material.

Property	Typical value
Density (g/cm^3)	1.03
Tensile strength (MPa)	32
Strain at break (%)	9
Tensile modulus (GPa)	1.8
Printing temperature (°C)	220–240
Melting temperature (°C)	245 ± 10

TABLE 16.4 Mechanical properties of PLA material.

Property	Typical value
Density (g/cm^3)	1.24
Tensile strength (MPa)	60
Strain at break (%)	9
Tensile modulus (GPa)	3.1
Printing temperature (°C)	190–210
Melting temperature (°C)	160 ± 10

16.2.1.4.3 Polymethyl methacrylate

Polymethyl methacrylate (PMMA) or acrylic is a rigid thermoplastic material mostly used as an economical substitute to glass having many advantages as compared to other transparent plastics such as high UV resistance, excellent light transmission, and a wide selection of colors. PMMA is also used for many biomaterial applications such as bone cement, lenses, drug delivery systems, bone substitutes, hip joint transplantation, etc., due to its inert properties. For dental applications, PMMA is used as a substitute for missing dental roots due to its mechanical properties similar to dentine. Table 16.5 shows the mechanical properties of PMMA material.

16.2.1.4.4 Polyamide

Polyamide (PA) or Nylon is an engineering plastic commonly used in mechanical applications due to its, rigidity, high load-bearing capacity, and good mechanical properties. This plastic is easy of finishing mechanically and is widely used as a substitute for bronze, brass, aluminum in industries, and agricultural applications. It absorbs moisture, thus not recommended to use in water as it may impose changes in dimensions. Different types of PAs are PA 6, PA 12, PA 66, PA 69, and PA 46. Table 16.6 shows the mechanical properties of PA.

TABLE 16.5 Mechanical properties of PMMA material.

Property	Typical value
Density (g/cm^3)	1.185
Tensile strength (MPa)	75
Compressive strength (MPa)	117.5
Strain at break (%)	4.5
Tensile modulus (GPa)	2.85
Printing temperature (°C)	245–255

TABLE 16.6 Mechanical properties of PA 6 material.

Property	Typical value
Density (g/cm^3)	1.13
Tensile strength (MPa)	66.5
Compressive strength (MPa)	68
Strain at break (%)	210
Tensile modulus (GPa)	2.4
Printing temperature (°C)	250–270

16.2.1.4.5 Polycaprolactone

Polycaprolactone (PCL) is a biodegradable semicrystalline material having low melting point of 60°C and glass transition temperature of −60°C. PCL was first synthesized by ring polymerization process in 1930s. PCL is highly hydrophobic, thus has longer degradation time than PLA material, making it suitable for application with longer degradation time. Mechanical processing of PCL material is relatively easy by conventional melting techniques, and can be filled with additives and fillers to improve mechanical properties. PCL scaffolds are used for tissue engineering of bones and cartilage applications.

16.2.1.5 High-performance plastics

There are some plastic materials that are used in some advanced applications. These materials have superior properties than that of common plastic materials. Some of the advanced engineering plastics are presented below.

16.2.1.5.1 Polyether ether ketone

Polyether ether ketone (PEEK) is a semicrystalline thermoplastic that shows excellent mechanical, chemical, rheological, and electrical properties as compared to general used plastic that can be used for various applications such as biomedical implants, wear resistance components, high thermal properties is required [3–5]. The cost of the PEEK material is quite high; researchers have tried various PEEK polymers composites for specific applications.

The high thermal stability of PEEK enables the material to be used continuously at a high temperature of up to 250°C for a quite long time. PEEK also exhibits good combustion resistance, thus produces fewer gases when burned, and provides good resistance to X-rays and Beta and gamma rays [4]. PEEK composites can be used for manufacturing high-temperature resistance industrial components, aircraft, spacecraft, satellite components, etc. Researchers have tried various additives with PEEK polymer matrix which are listed in Table 16.7.

Although PEEK seems promising material, and has some difficulties while 3D printing which needs to be taken care of. During 3D printing of PEEK, due to accumulation of high thermal stresses, warpage and layer delamination can be observed affecting dimensional accuracy and mechanical properties [9]. Mechanical properties of PEEK are listed in Table 16.8.

TABLE 16.7 Different PEEK composites and corresponding effects.

PEEK composite	Result/Effect	Reference
PEEK/MWCNT	Improvement in impact and tensile strength, whereas failure strain is decreased	[6]
PEEK/Carbon fiber	Improvement in flexure strength and laminar shear strength	[5]
PEEK/Nano diamond particle	Improvement in thermal conductivity	[7]
PEEK/Pitch-based carbon fiber	Improvement in crystallinity	[8]

TABLE 16.8 Mechanical properties of PEEK material [10].

Property	Typical value
Density (g/cm^3)	1.3
Melting temperature (°C)	343
Glass transition temperature (°C)	143
Coefficient of thermal expansion (ppm/k)	Average below Tg: 55 Average above Tg: 140
Heat deflection temperature (°C)	152
Thermal conductivity (W/m.k)	0.32
Young's modulus (GPa)	4
Tensile strength (MPa)	100
Elongation at break (%)	45
Flexural modulus (GPa)	3.9
Flexural strength (MPa)	162
Compressive modulus (GPa)	3.2
Compressive strength (MPa)	125
Hardness (Shore D)	84.5
Water absorption (%)	0.45
Flammability	V-0

16.2.1.5.2 Polyphenylene Sulfide

Polyphenylene sulfide (PPS) is a semicrystalline thermoplastic with excellent mechanical and rheological properties, high thermal stability, excellent chemical and flame resistance, and high impact resistance, having wide applications in various industrial applications such as automobile, aerospace components, electronic devices, chemical containers, etc. PPS has better compressive strength as compared to PEEK material. PPS shows improved mechanical properties when mixed with additives to form composite material for specific applications.

PPS is a new material for 3D printing; very few data related to 3D printing parameters are recorded to date. In order to print PPS, rheological and thermal properties analysis is needed to find 3D printing process parameters. 3D printing of PPS is quite challenging due to its complex print parameters, material properties, and temperature profile. Mechanical properties of PPS material are shown in Table 16.9 [11].

TABLE 16.9 Mechanical properties of PPS.

Property	Typical value
Density (g/cm^3)	1.35
Melting temperature (°C)	280
Dielectric strength (kV/cm)	220–280
Coefficient of thermal expansion (/°C)	$51.6–97.9 \times 10^{-6}$
Thermal conductivity (W/m.k)	0.22
Electrical conductivity (S/cm)	1.5×10^{-16}
Vickers microhardness (kg/cm^2)	0.24

TABLE 16.10 Different mechanical properties of PEI.

Property	Typical value
Density (g/cm^3)	1270
Melting temperature (°C)	354
Dielectric strength (kV/cm)	190–300
Coefficient of thermal expansion (/°C)	54–56 × 10^{-6}
Thermal conductivity (W/m.K)	0.22
Electrical conductivity (S/cm)	1.5 × 10^{-16}
Rockwell hardness (R Scale)	R115–R120

16.2.1.5.3 Polyetherimide

Polyetherimide (PEI) is an important high-temperature amorphous thermoplastic having high strength to weight ratio, excellent mechanical and electrical insulation properties, flame retardant, and excellent chemical resistance, which has been developed to overcome the challenges of polyimides. PEI can be widely used for applications such as aerospace and automotive industries, electrical components, reusable and disposable medical applications, and metal replacement material due to its high strength to weight ratio. 3D printing of PEI is quite difficult, due to its complex thermal profile. Very few studies related to 3D printing and mechanical properties of PEI material are available, most of them have considered only a few process parameters. A lot of research is still needed to be done to optimize the 3D printing process parameters of PEI material [12]. Mechanical properties of PEI are listed in Table 16.10.

Out of all the available polymers, thermoplastic and elastomers have wide applications in extrusion-based 3D printing techniques. Some of the researchers have also investigated the use of advanced engineering plastics through 3D printing.

16.2.2 Elastomers

Copolymers or compounds of thermoplastic and elastomers are known as thermoplastic elastomers (TPEs). Macromolecular structure with the altered hard and soft segment is a major factor responsible for the elasticity of TPE. A decrease in mechanical properties can be noted with the rise in temperature due to thermoplastic behavior. Main families of TPEs can be classified in the pyramid of excellence as shown in Fig. 16.2.

16.2.2.1 Ethylene vinyl acetate

Ethylene vinyl acetate (EVA) is an elastomeric material having vinyl acetate content varying from 40% to 60%, cross-linked using perioxide and radiation methods. Polymerization technique also varies the VA content in EVA having excellent resistance to oxygen, ozone, and light and poor resistance to wear and tear. It is mainly used for cable applications and medical extrusion.

16.2.2.2 Thermoplastic polyurethane

Thermoplastic polyurethane (TPU) is a TPE, having high flexibility and durability. It has characteristic properties of plastic and rubber offering several benefits over other elastomers due to its excellent tensile strength, excellent load-bearing capacity, and high elongation at break. TPU is mainly used in automotive applications, wires and cables, wearable devices, textile clothing, etc. Table 16.11 shows the mechanical properties of TPU material.

16.2.3 Thermosetting

Thermosetting plastics are widely used for day-to-day applications due to their design and manufacturing flexibility and desirable combination of properties. Thermosets are 3D structured cross-linking polymers obtained after the heating or curing process. These polymers have good fire resistance and chemical resistance. They show better creep behavior as the link between chains has restricted displacement. Usually, thermosets are processed in the form

FIGURE 16.2 Elastomers available for different applications.

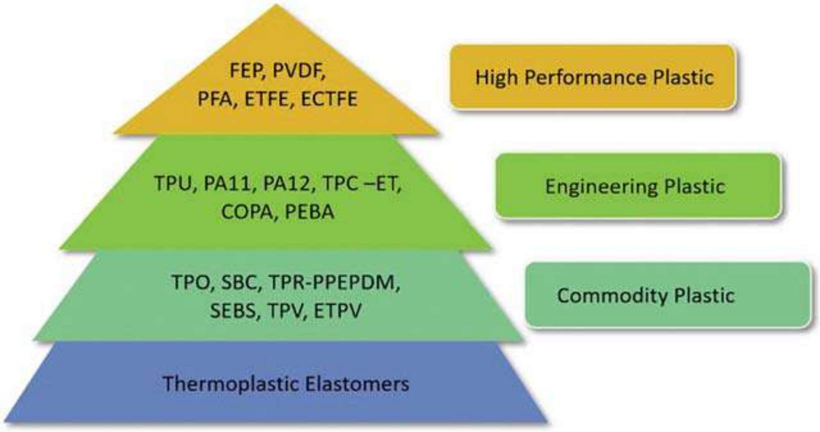

TABLE 16.11 Mechanical properties of TPU material.

Property	Typical value
Density (g/cm^3)	1.17
Hardness (Shore A)	67
Tensile strength (MPa)	20
Elongation at break (%)	700
100% modulus at strain 100% (MPa)	2.99
Printing temperature (°C)	210–230

of resins. Thermoset resins are usually insoluble in most of the inorganic solvents and are processed in three stages. In the first stage, the resin is in the insoluble and fusible stage and is commonly known as resole stage; in the second stage, the resin is partially soluble; and in the third stage, a cross-linked reaction gives the final structure of thermoset polymer. One of the main properties of thermosets is that, once the polymer is hardened during curing or heating process, it cannot soften. Due to this, it is impossible to use thermosets for pellet-based 3D printing applications.

16.3 Pellet feeding methods for 3D printing

In extrusion-based 3D printing systems, the material is deposited through a nozzle onto a platform to make 3D parts. In filament-based 3D printing systems, raw material is fed in the form of the filament into a liquefier where it is fused and extruded using a CNC controlled nozzle (X–Y direction) onto movable (Z-direction) build platform. Literature suggests that the filament feeding method has been become popular due to its simplicity, reliability, and easy control. Nevertheless, various issues are associated with this kind of feeding method. One of the issues is the material to be used must have enough stiffness and compressive strength for proper feeding of the filament inside the liquefier without any interruption. As the pellets offer various benefits over the filament, various efforts have been made toward the development of a system for the direct processing of pellets. The screw and plunger driven feeding systems were evolved as the methods of transforming pellets into the continuous filament. The principle of screw and plunger extrusion–based 3D printing systems is discussed below.

16.3.1 Plunger extrusion principle–based 3D printing systems

In these types of systems, the reservoir and plunger are used as primary parts. In the beginning, a reservoir/cylinder is filled up with the material where it is heated at an appropriate temperature. Once the material is reached a

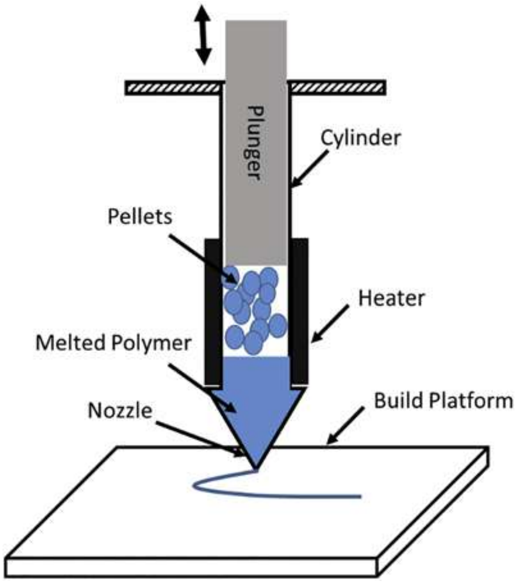

FIGURE 16.3 Schematic of plunger extrusion principle–based 3D printing.

semiliquid state, the plunger pushes the material against the small nozzle opening in the form of thin wire. The nozzle moves in *XY* directions to create a layer. Furthermore, layers are added until the part fabrication is completed. The schematic representation of this system is presented in Fig. 16.3.

16.3.2 Screw extrusion principle–based 3D printing systems

In these types of systems, the material is processed with the help of screw and barrel assembly. A rotating screw is used to create the required pressure for the extrusion. The material is fed by using the funnel into a barrel where heat is provided to soften the material. Further, softened material is extruded from a nozzle into the wire shape profile. The schematic representation of this system is presented in Fig. 16.4.

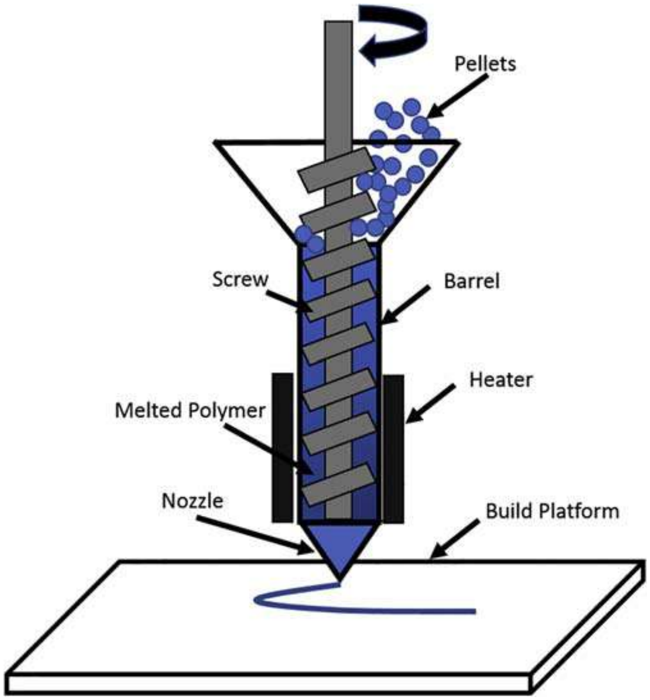

FIGURE 16.4 Schematic of screw extrusion principle–based 3D printing.

The application potential of the plunger-driven 3D printing systems is found in various applications. These systems are simple to operate but the discontinuous extrusion of the material makes it ineffective for fabricating the larger objects. While on the other hand, a screw-driven 3D printing system could feed the material continuously with the help of a rotating screw.

16.4 3D printers for pellets

There are known technical solutions for Fused Granules Fabrication (FGF) printing. In literature, few studies have been found on it [13–20]. The FGF process has been used by a group of researchers to print pellet form of materials [21]. A detailed description of this process is given below.

16.4.1 *Fused Granules Fabrication*

FGF is a process similar to the FFF process in which pellets are used as feed material instead of filament. Extrusion mechanism in FGF process is relatively simple as plastic extrusion mechanism uses robust barrel and extrusion system. Pellets are gravity fed in the feeder section, which are then passed into a heated barrel through a screw that is driven by a servo or stepper motor. The barrel has multiple heated sections, such as the feeding section, metering section, and compression section, where the material is heated gradually and melts. The melted material is then extruded from the nozzle and part can be printed (as shown in Fig. 16.5). The capability of FGF was compared with FFF by considering the same process parameters, as shown in Table 16.12.

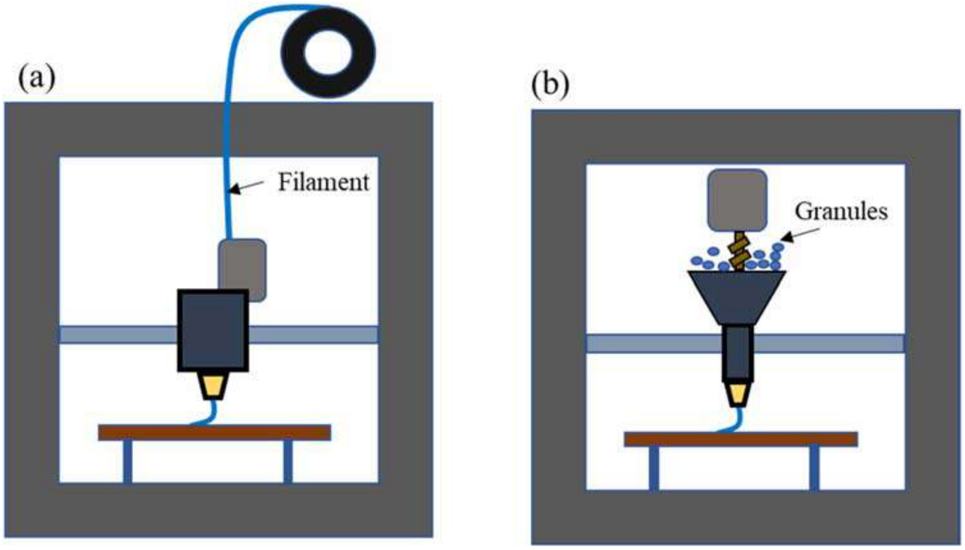

FIGURE 16.5 Schematic representation of (A) FFF and (B) FGF.

TABLE 16.12 Comparison of FFF and FGF.

Selected parameters	Values
Layer thickness	0.2 mm
Platform temperature	60 °C
No. of contours	3
Solid layers from top	3
Solid layers from bottom	3
Infill density	100%
Deposition pattern	0/90°
Max deposition speed	140 mm/s for FFF 40 mm/s for FGF
Nozzle diameter	Two values considered 0.5 and 0.8 mm for FFF Only 0.8 mm considered for FGF

16.4.2 *Commercially available printers for pellet printing*

There are various commercially available pellet extruders available in the market. The main advantage of using pellet extruder over filament extruder is pellet extrusion that can be used for large size printers, and since it directly prints from the pellet, it is easy to mix additives and print composite materials. Table 16.13 shows different commercially available pellet extruders.

TABLE 16.13 Commercially available pellet-based 3D printers.

Make	Model	Size	Country of origin	Websites
Juggerbot3D	Tradesman Series P3-44	915 mm × 1220 mm × 1220 mm	US	https://juggerbot3d.com/
Titan Robotics Ltd	Atlas 1.0	762 mm × 762 mm × 1143 mm	US	https://titan3drobotics.com/
DYZE design	Pulsar	Manufactures compatible pellet extruder for most of FFF printer	Canada	https://dyzedesign.com/
IT3D Group	Tumaker NX Pro	290 mm × 180 mm × 200 mm	Spain	https://it3d.com/en/
Direct3D	Direct3D pellet extruder	Manufactures compatible pellet extruder for most of FFF printer	Italy	https://www.direct3d.it/
Cosine	Cosine AM1 3D printer	1753 mm × 1474 mm × 1855 mm	US	https://www.cosineadditive.com/en/home/

16.4.3 *Commercial polymers for 3D printing*

3D printing generates lots of waste due to print failure and printed support material. Since 3D printing is mainly used for design validation, many prototypes are discarded or disposed of postdesign verification. With the growing application of 3D printing, thermoplastic wastage is also going to increase. The solution to the thermoplastic wastage can be making filament from this wastage or pellet 3D printing using the melt extrusion process. Granules obtained from a virgin polymer or recycled polymer will be converted into small strands of standard diameter under the influence of temperature and pressure. So far, very little information is available about the mechanical properties of recycled plastics [22].

Different types of materials are available in the commercial market in the pellet form. The potential of these materials has been identified using injection mold—based extrusion systems. However, only a limited number of materials have been explored by researchers in the domain of 3D printing. Table 16.14 presents the list of the most common commercially available materials in pellet form.

16.5 Process of creating pellets from polymer waste

The most common groups of polymers that are currently recycled are ABS, PC, PP, PVC, HDPE, LDPE, etc. Literature reviews that this thermoplastic has the potential to be used for 3D printing. However, most of the research overviews the potential of using PLA material for recycling. The effect of multiprocessing of polymer material is studied by Zenkiewicz et al. [23]. Effect of adding additives in thermoplastic for improved strength is studied by Pillin et al. [24] and Gkartzou et al. [25]. Recycling of polymer material consists of the following stages segregation and washing; the material is then extruded into filament which can be used for 3D printing by feeding into the 3D printer. Additional stages appear when any material modification is needed.

16.5.1 *Process of converting waste into pellets*

There are various ways to recycle plastic, and difficulties in recycling depend upon the polymer used, packaging, and product type. For example, rigid container boxes made up of single polymer and package are simpler to recycle than a container made up of multimaterial polymers. Thermoplastics such as ABS, PP, and PET have high compatibility for mechanical recycling. The ability to use recycled plastic instead of virgin polymer depends upon the purity and mechanical properties of a recycled polymer. This led to the current recycling process quite easily separable

TABLE 16.14 Commonly available materials in pellet form for possible use in pellet 3D printing.

Name	Abbreviation	Type
Acrylonitrile butadiene styrene	ABS	Thermoplastic
Polylactic acid	PLA	Thermoplastic
High-density polyethylene	HDPE	Thermoplastic
Low-density polyethylene	LDPE	Thermoplastic
Polypropylene	PP	Thermoplastic
Polystyrene	PS	Thermoplastic
Polyamide	PA	Thermoplastic
Polyethylene terephthalate	PET	Thermoplastic
Polyvinyl chloride	PVC	Thermoplastic
Polyether ether ketone	PEEK	Thermoplastic
Polyvinylidene fluoride	PVDF	Thermoplastic
Polyethersulfone	PES	Thermoplastic
Polycaprolactone	PCL	Thermoplastic
Ethylene vinyl acetate	EVA	Thermoplastic elastomers (TPEs)
Polyolefin blends	TPE-O	TPEs
Polyolefin alloys	TPE-V	TPEs
Styrene	TPE-S	TPEs
Styrene-ethylene/Butylene-styrene	SEBS	TPEs
Polyurethane	TPE-U	TPEs
Polyester	TPE-E	TPEs

FIGURE 16.6 Process of waste conversion into pellets.

plastic packages such as plastic bottles (PET) and milk bottles (HDPE), which can be easily segregated from multi-material mix waste streams. The process of plastic recycling comprises several important stages: collection, sorting and cleaning, shredding and resizing, separation, and/or compatibilization to reduce contamination from incompatible polymers (Fig. 16.6).

16.5.1.1 *Collection and distribution of plastics*

The first stage of recycling is the collection of plastic materials from home, institutes, industries, waste collection centers, etc., which can be done by either private vendors or government vendors. Another point of collections can be common collection centers or nodal points such as recycling bins or recycling facilities.

16.5.1.2 *Sorting and cleaning*

The second stage in plastic recycling is sorting and cleaning. There can be several different types of plastics that need to be segregated from each other. Plastics can be separated based on physical appearances, thickness, colors, etc. Postseparation plastic is cleaned and washed to remove any present impurities, the presence of which can reject the entire batch of recycled plastic.

16.5.1.3 *Shredding and resizing*

Cleaned and sorted plastic is then shredded into small pieces. These small pieces may be comprised of metallic impurities which can be further processed in the next stage. Breaking into small pieces makes it easy in the identification of remaining impurities.

16.5.1.4 *Separation*

Small plastic pieces are then separated based on density and thickness. Shredded plastic is floated in the container of water where plastics can be separated from other metallic impurities, followed by an air classification test, where lighter plastic is separated from heavier ones.

16.5.1.5 *Extrusion and compounding*

This is the final step of the recycling process where the material is extruded in the form of pellets or transformed into a finished product directly. Additives of fillers can be added during the extrusion process to improve the mechanical properties of recycled plastic to meet end product requirements.

16.6 Compounding of polymer pellets for improved material properties

During extrusion, the polymer degrades due to shear stress, oxygen, and uncertain temperature profile which impact the physical properties of the polymer, influencing high quality of the extrusion products [22]. Repeated extrusion strongly influences the molecular weight, viscosity, and breaking strength of the polymer. Change in properties is greatly dependent on factors such as temperature and repeated extrusion of the same polymer [23]. Various compounding methods have been adopted in order to overcome this issue and to enhance the material properties. In literature, various additives are used to improve the molecular weight, physical and rheological properties of virgin, and reprocessed polymers that have been studied by researchers. Addition of biopolymer in PLA matrix increases the melting properties, whereas tensile and Young's odulus are decreased by 18% and 6%, respectively [25]. Addition of carbon fiber in reprocessed PLA matrix improves the bending strength by 25% [26]. Hydroquinone and tropolone are used as oxidizing stabilizers, capturing free radicals, and improving chain length during the thermal extrusion process, thus improving the mechanical properties of PLA material [24]. Additives in the form of biocarbon can significantly improve the mechanical properties of reprocessed PET bottles, improving tensile strength and Young's modulus by 32% and 60%. The use of biocarbon in PLA matrix improves stiffness of the material by 8% [27]. Another attempt to improve the properties of reprocessed polymers is by adding crystalline powders such as Fe, Si, Cr, and Al into PP and HDPE polymers. Addition of 1% nanocrystalline powder of Fe—Si—Cr or Fe—Si—Al can improve yield strength and Young's modulus by 37% and 17% and also reduces crack formation [28]. Mixing of SiC/Al_2O_3 in reprocessed HDPE improves the mechanical strength of the material, whereas it slightly affects the thermal properties of the base material. Paraffin wax can be used as a binding agent during the mixing process [29]. The addition of filler material or additives can significantly improve the mechanical properties of reprocessed material, thus enables to use them for end application purposes (Table 16.15).

It can be seen that additives can improve the physical and other properties of polymers. However, there are various factors that may affect the performance of fabricated parts made of compounded materials. The factors and their role are discussed in Sections 16.6.1—16.6.4.

16.6.1 *Role of compounding method*

The method adopted for compounding also plays an important role in the performance of the fabricated part [30—32]. Compounding is done primarily with one of three different types of compounders, namely, single screw extruders, twin-screw extruders, and cokneaders [33]. The methods can be used for short fibers and long fibers such as glass fibers. However, certain fibers may agglomerate at the entrance of hopper, thereby affecting the compounding process. In such cases, kneading can be used. Before molding, the polymer is mixed with the fiber during the kneading phase. After that, the mixed substance is granulated, and specimens are prepared [34].

TABLE 16.15 Various polymers with additives and effects.

Polymer matrix	Additives	Effect	References
PLA	Biopolymer	Decreases tensile strength by 18% and Young's modulus by 6%	[25]
PLA	Carbon fiber	Improves bending strength by 25%	[26]
PLA	Hydroquinone and tropolone	Improves oxidizing stabilizers	[24]
PET	Carbon fiber	Improves tensile strength and young's modulus by 32% and 60%.	[27]
PP and HDPE	Fe–Si–Cr or Fe–Si–Al	Improve yield strength and Young's modulus by 37% and 17%	[28]
HDPE	SiC/Al_2O_3	Improves mechanical strength	[29]

16.6.2 Role of processing temperature

Moreover, the processing temperature during the pelletizing stage and fabrication of samples is also important and can significantly affect the compounding. Fig. 16.7 illustrates the effect of temperature on interfacial bonding.

The first problem in making nanocomposites with layered structured nanomaterials is uniform dispersion. A diameter in microns has to be dispersed into millions of nanometer-thick platelets (intercalate and exfoliate) as in the case of nanoclay.

16.6.3 Role of introduction stage of additives

Additives can be introduced to the polymer in various ways, such as adding the filler in unmelted polymer pellets. Another way is to add some portion of filler first and the remaining is added in a melted polymer. Adding the filler in unmelted pellets can be effective; however, it can wear out the screw if they are of abrasive nature. Moreover, if the fillers have low bulk density, then they can cause an issue of agglomeration and affect its dispersion, thereby influencing the compounding process. Prevention of agglomeration is a critical issue and needs to be controlled. Homogeneity has to be achieved by controlling the process. Fig. 16.8 shows the important factors affecting the compounding and dispersion of fillers in the polymer matrix. First, the agglomerates have to break down into tactoids. The agglomerates after separation are distributed randomly inside the polymer matrix. This is now determined by the overall level of shear strain imposed. This distribution now is not affected by the magnitude of shear stress.

16.6.4 Role of pellet and filler size on compounding

The size of both the pellets and fillers also plays an important role in dispersion. The aggregation of the filler is possible when it is premixed with polymer pellets in a hopper due to the size difference between the two ingredients.

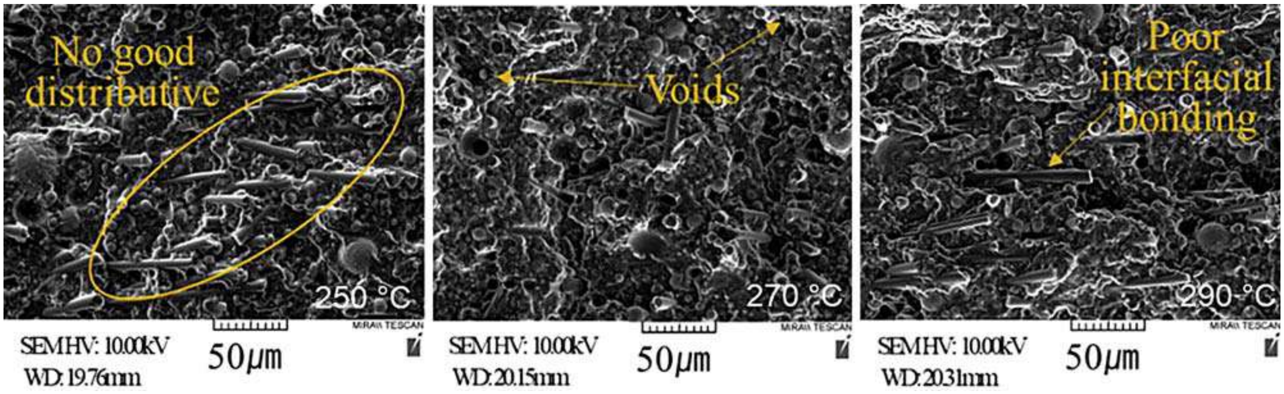

FIGURE 16.7 Effect of temperature on interfacial bonding. *This figure is reprinted with permission from Ref. [35], Copyright (2019) Creative Commons Attribution License.*

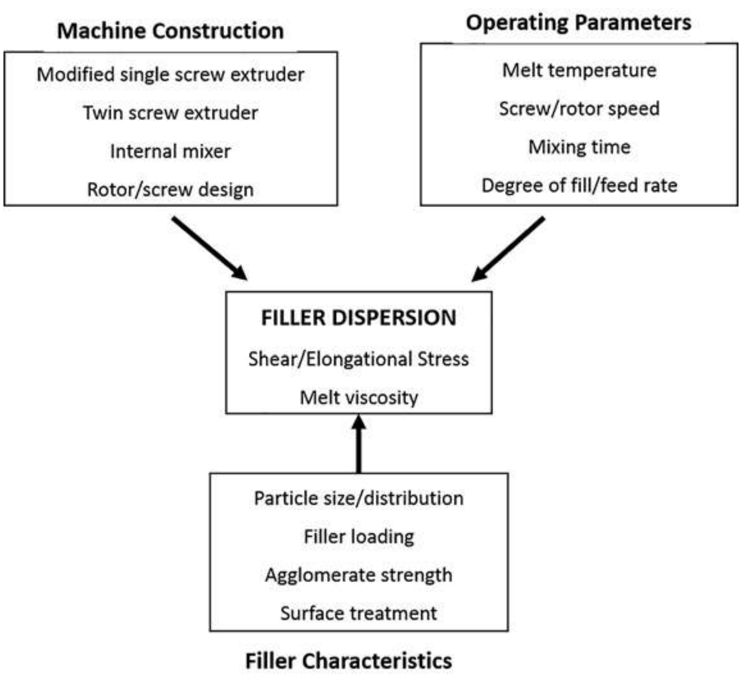

FIGURE 16.8 Important factors for consideration while compounding. *This figure is reprinted with permission from Ref. [36], Copyright (2017) Springer Cham.*

The same is illustrated in Fig. 16.9. It can be seen that for pellets and filler the size difference can be significant that may lead to dispersion issues. On the contrary, if the polymer powder is used the same difference can be brought down. This shows the limitation of pellet compounding over the use of powder. The filler can accumulate at the surface of the compounding equipment during melting. This can be reduced by remixing pellets and fillers of identical geometry. Remixing can enhance the interaction between the polymer and the fillers thus ensuring better compounding. Finally, it leads to enhance the performance of fabricated parts.

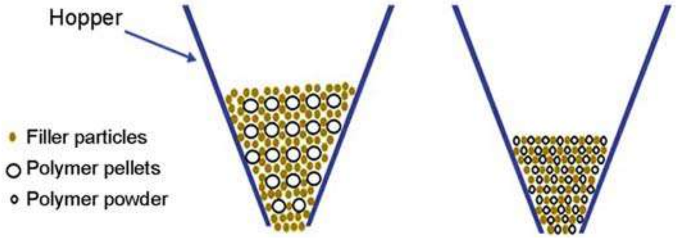

FIGURE 16.9 Particle size difference between pellets and filler. *This figure is reprinted with permission from Ref. [37], Copyright (2021) Springer Nature.*

16.7 Summary

Various polymeric materials available in pellet form were presented along with their processability with pellet-based 3D printing systems. Screw and plunger extrusion—based principles were presented for processing the pellets. Screw extrusion—based 3D printing systems have been revealed as most effective for larger objects fabrication due to the capability of continuous extrusion of material. Furthermore, a discussion on the conversion of waste material into pellets has also been presented. Compounding of pellets has also been elaborated with the consideration of significant factors and their role on performance measures.

In future, the potential of unexplored pellets may also be analyzed using a pellet-based 3D printing system. Currently, literature reports different variants of pellet-based 3D printing systems. Most of them are focused on system development and part fabrication; however, they do not provide insight information about the material degradation, filament uniformity, and the part quality. These aspects of pellet-based 3D printing may be covered in further research works.

References

[1] S.K. Gawali, N. Kumar, P.K. Jain, Investigations on the development of heated build platform for additive manufacturing of large-size parts, in: Manufacturing Engineering. Lecture Notes on Multidisciplinary Industrial Engineering, Springer, Singapore, 2020, https://doi.org/10.1007/978-981-15-4619-8_1.

[2] M. Vispute, N. Kumar, P.K. Jain, P. Tandon, P.M. Pandey, Shrinkage compensation study for performing machining on additive manufactured parts, Mater. Today Proc. 5 (9) (2018) 18544–18551.

[3] W. Wu, P. Geng, G. Li, D. Zhao, H. Zhang, et al., Influence of layer thickness and raster angle on the mechanical properties of 3D-printed PEEK and a comparative mechanical study between PEEK and ABS, Materials 8 (9) (2015) 5834–5846.

[4] M. Thiruchitrambalam, D.B. Kumar, D. Shanmugam, M. Jawaid, A review on PEEK composites – manufacturing methods, properties and applications, Mater. Today Proc. 33 (2020) 1085–1092.

[5] L. Pan, U. Yapici, A comparative study on mechanical properties of carbon fiber/PEEK composites, Adv. Compos. Mater. 25 (4) (2016) 359–374.

[6] H. Cheng, M. Chen, Effect of functionalization of multiwalled carbon nanotubes with aminated poly(ether sulfone) on thermal and mechanical properties of poly(ether ether ketone) nanocomposites, High Perform. Polym. 29 (7) (2017) 857–868.

[7] Z. Wahab, Z.M. Marsh, A. Tessema, A. Kidane, M. Stefik, et al., Effect of nanodiamond (ND) surface functionalization on the properties of ND/PEEK composites, IEEE Trans. Compon. Packag. Manuf. Technol. 7 (2) (2017) 165–177.

[8] A. Martin, F. Addiego, G. Mertz, J. Bardon, D. Ruch, et al., Pitch-based carbon fibre-reinforced PEEK composites: optimization of interphase properties by water-based treatments and self-assembly, J. Mater. Sci. Eng. 05 (06) (2016) 1–9.

[9] A.R. Zanjanijam, I. Major, J.G. Lyons, U. Lafont, D.M. Devine, Fused filament fabrication of peek: a review of process-structure-property relationships, Polymers 12 (8) (2020).

[10] S. Singh, C. Prakash, S. Ramakrishna, 3D printing of polyether-ether-ketone for biomedical applications, Eur. Polym. J. 114 (January) (2019) 234–248.

[11] A.S. Rahate, K.R. Nemade, S.A. Waghuley, Polyphenylene sulfide (PPS): state of the art and applications, Rev. Chem. Eng. 29 (6) (2013) 471–489.

[12] A.W. Gebisa, H.G. Lemu, Influence of 3D printing FDM process parameters on tensile property of ultem 9085, Procedia Manuf. 30 (2019) 331–338.

[13] N. Kumar, P.K. Jain, P. Tandon, P.M. Pandey, The effect of process parameters on tensile behavior of 3D printed flexible parts of ethylene vinyl acetate (EVA), J. Manuf. Process. 35 (2018) 317–326.

[14] N. Kumar, P.K. Jain, P. Tandon, P.M. Pandey, Extrusion-based additive manufacturing process for producing flexible parts, J. Brazilian Soc. Mech. Sci. Eng. 40 (3) (2018) 1–12.

[15] N. Kumar, S. Shaikh, P.K. Jain, P. Tandon, Effect of fractal curve based toolpath on part strength in fused deposition modelling, Int. J. Rapid Manuf. 5 (2015) 186–198.

[16] N. Kumar, P.K. Jain, P. Tandon, P.M. Pandey, 3D printing of flexible parts using EVA material, Mater. Phys. Mech. 37 (2) (2018) 124–132.

[17] N. Kumar, P.K. Jain, P. Tandon, P.M. Pandey, Additive manufacturing of flexible electrically conductive polymer composites via CNC-assisted fused layer modeling process, J. Brazilian Soc. Mech. Sci. Eng. 40 (4) (2018) 175.

[18] N. Kumar, P.K. Jain, P. Tandon, P.M. Pandey, Toolpath generation for additive manufacturing using CNC milling machine, in: L.J. Kumar, P.M. Pandey, D.I. Wimpenny (Eds.), 3D Printing and Additive Manufacturing Technologies, Springer, Singapore, 2019, pp. 73–82.

[19] N. Kumar, P.K. Jain, P. Tandon, P.M. Pandey, Investigation on the effects of process parameters in CNC assisted pellet based fused layer modeling process, J. Manuf. Process. 35 (2018) 428–436.

[20] N. Kumar, P.K. Jain, P. Tandon, P.M. Pandey, Additive manufacturing of flexible electrically conductive polymer composites via CNC-assisted fused layer modeling process, J. Brazilian Soc. Mech. Sci. Eng. 40 (4) (2018) 1–13.

[21] A. Alexandre, F.A.C. Sanchez, H. Boudaoud, M. Camargo, J.M. Pearce, Mechanical properties of direct waste printing of polylactic acid with Universal pellets extruder: comparison to fused filament fabrication on open-source desktop three-dimensional printers, 3D Print. Addit. Manuf. 7 (5) (2020) 237–247.

[22] I. Anderson, Mechanical properties of specimens 3D printed with virgin and recycled polylactic acid, 3D Print. Addit. Manuf. 4 (2) (2017) 110–115.

[23] M. Żenkiewicz, J. Richert, P. Rytlewski, K. Moraczewski, M. Stepczyńska, et al., Characterisation of multi-extruded poly(lactic acid), Polym. Test. 28 (4) (2009) 412–418.

[24] I. Pillin, N. Montrelay, A. Bourmaud, Y. Grohens, Effect of thermo-mechanical cycles on the physico-chemical properties of poly(lactic acid), Polym. Degrad. Stabil. 93 (2) (2008) 321–328.

[25] E. Gkartzou, E.P. Koumoulos, C.A. Charitidis, Production and 3D printing processing of bio-based thermoplastic filament, Manuf. Rev. 4 (2017).

[26] X. Tian, T. Liu, Q. Wang, A. Dilmurat, D. Li, et al., Recycling and remanufacturing of 3D printed continuous carbon fiber reinforced PLA composites, J. Clean. Prod. 142 (2017) 1609–1618.

[27] M. Idrees, S. Jeelani, V. Rangari, Three-dimensional-printed sustainable biochar-recycled PET composites, ACS Sustain. Chem. Eng. 6 (11) (2018) 13940–13948.

[28] G.-T. Pan, S. Chong, H.-J. Tsai, W.-H. Lu, T.C.-K. Yang, The effects of iron, silicon, chromium, and aluminum additions on the physical and mechanical properties of recycled 3D printing filaments, Adv. Polym. Technol. 37 (4) (2018) 1176–1184.

[29] N. Singh, R. Singh, I.P.S. Ahuja, Recycling of polymer waste with SiC/Al_2O_3 reinforcement for rapid tooling applications, Mater. Today Commun. 15 (2018) 124–127.

[30] V. Francis, P.K. Jain, Achieving improved dielectric, mechanical, and thermal properties of additive manufactured parts via filament modification using OMMT-based nanocomposite, Prog. Addit. Manuf. (2017) 1–7.

[31] V. Francis, P.K. Jain, Experimental investigations on fused deposition modelling of polymer-layered silicate nanocomposite, Virtual Phys. Prototyp. 11 (2) (2016) 109–121.

[32] V. Francis, P.K. Jain, Investigation on the effect of surface modification of 3D printed parts by nanoclay and dimethyl ketone, Mater. Manuf. Process. 6914 (November) (2017) 1–13.

[33] N. Kumar, P.K. Jain, P. Tandon, P.M. Pandey, Investigations on the melt flow behaviour of aluminium filled ABS polymer composite for the extrusion-based additive manufacturing process, Int. J. Mater. Prod. Technol. 59 (3) (2019) 194–211.

[34] N.M. Barkoula, S.K. Garkhail, T. Peijs, Effect of compounding and injection molding on the mechanical properties of flax fiber polypropylene composites, J. Reinforc. Plast. Compos. 29 (9) (2010) 1366–1385.

[35] Y.S. Kim, J.K. Kim, E.S. Jeon, Effect of the compounding conditions of polyamide 6, carbon fiber, and Al_2O_3 on the mechanical and thermal properties of the composite polymer, Materials 12 (18) (2019) 1–14.

[36] P.R. Hornsby, Compounding of particulate-filled thermoplastics, in: R. Rothon (Ed.), Fillers for Polymer Applications. Polymers and Polymeric Composites: A Reference Series, Springer, 2017, p. 489.

[37] M.M.A. Nassar, K.I. Alzebdeh, T. Pervez, N. Al-Hinai, A. Munam, et al., Polymer powder and pellets comparative performances as bio-based composites, Iran. Polym. J. 30 (3) (2021) 269–283.

CHAPTER

17

Films for sheet lamination

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17.1 Introduction

Materials used in the sheet lamination (SHL) are paper, polymers (poly(vinyl chloride), PVC), metals (aluminum, copper, stainless steel, and titanium), ceramics (alumina, silicon nitride, and zirconia), textiles, and composites (prepregs). The material that enters the SHL process is first made by classical processing and must be in the form of a film, foil, or plate. Of the pure polymer materials, only PVC has been used since the beginning of SHL application, and more recently also polymer composites (thermoplastics reinforced with fibers). The main reason for the application of PVC in the SHL process is in its simple production as a thin film, low cost, and the possibility of easy gluing with water-based glue (lamination process). Other polymer materials used in the SHL process are polymer composites in the form of the prepreg. The introduction of prepregs in additive manufacturing was to improve the properties of polymer materials by adding fibers as reinforcements. In this chapter, only two systems used in the SHL process will be described, namely PVC and polymer composites.

17.2 Poly(vinyl chloride)

17.2.1 Introduction to poly(vinyl chloride)

PVC with polyolefins (polyethylene (PE), polypropylene (PP), and their blends) and polystyrene (PS) belongs to the group of commodity thermoplastic materials. Their low cost, excellent performance, and easy processability make PVC widely used thermoplastic material. PVC is an amorphous thermoplastic material characterized by absence of long-range order in structure (unordered structure). Since there is no long-range order in amorphous polymers there is also no change in the refraction index within material (within the range of light waves − wavelength 0.4−0.7 μm), so amorphous polymers that contain no pigments or fillers are transparent. Structure of the macromolecules in the solid and in molten state is the same (in contrast, crystalline or semicrystalline state always creates a new macromolecular order during cooling of the melt due to crystallization). The macromolecules form coils in the melt after cooling into the solid state. These coils have the same size whether they are in the melt or in the glassy state or individually dissolved in a chemically nonreactive solvent [1,2].

17.2.2 Chemical structure and synthesis

PVC is manufactured from vinyl chloride which is a gas at room temperature. Vinyl chloride monomer (VCM) is produced from the direct chlorination of ethylene and chlorine. Ethylene is derived from a cracking process involving feedstock based on oil or natural gas hydrocarbons, such as ethane, propane, or butane. The process involves catalysis at high temperatures and pressures to produce ethylene and other coproducts, such as propylene and butadiene. The ethylene is further processed to separate it from the coproducts. Chlorine is manufactured industrially, in the manufacture of caustic soda, by the cell electrolysis of salt water (saturated brine). Approximately 35% of Europe's chlorine production goes into PVC production. The three main electrolysis technologies for producing

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chlorine are: the membrane cell process, nowadays most widely used in Europe (61%); the mercury cell process, being phased out worldwide because of the toxic character of mercury; and the diaphragm cell process [3–5].

Respectively, there are two ways to manufacture VCM from ethylene (obtained from thermal cracking): the direct chlorination method and oxychlorination method. In the first stage of the reaction, 1,2-dichloroethane (EDC) is prepared by reacting ethylene with chlorine (obtained from electrolysis of salt) in either the vapor or the liquid phase. In a typical liquid phase process, reaction would be in the range 30–50°C in the presence of an iron chloride catalyst [4]. This reaction is shown in Ref. [4]:

$$CH_2 = CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$$

The crude 1,2-dichloroethane is washed with sodium hydroxide solution and then purified and dried by distillation. The dry 1,2-dichloroethane is then cracked to give VC [4]. This reaction is shown in Ref. [4]:

$$ClCH_2CH_2Cl \rightarrow CH_2 = CHCl$$

This is achieved by vaporizing the 1,2-dichloroethane and feeding through a series of tubes sited in a furnace. By adjustment of the temperature (in the range 300–600°C and typically about 530°C) and the residence time (about 20 s), a 40%–65% conversion may be obtained. The reaction product is then quenched rapidly to avoid decomposition and the monomer is isolated by fractional distillation. The particular feature of this process is that the hydrogen chloride formed during the dehydrochlorination stage and recovered during the purification is then used to generate more 1,2-dichloroethane by an oxychlorination reaction. In this process ethylene and hydrogen chloride gases are passed, with air, over a finely divided bed of copper(II) chloride supported on alumina [4]. This reaction is shown in Ref. [4]:

$$2CH_2 = CH_2 + 4HCl + O_2 \rightarrow 2ClCH_2CH_2Cl + 2H_2O$$

When EDC from the oxychlorination process is dehydrated and then thermally cracked (together with the EDC from the direct chlorination process), VCM is obtained. For many years, a major route to the production of VC was the addition of hydrochloric acid to acetylene in the presence of a mercuric chloride catalyst [4]. This reaction is shown in Ref. [4]:

$$CH = CH + HCl \rightarrow CH_2 = CHCl$$

Vinyl chloride is polymerized via free-radical polymerization in suspension (80%), bulk (10%), emulsion (10%–15%), and solution (1%) (Fig. 17.1) [3,4]. Today emulsion (and microsuspension) polymers are mainly used for paste applications, the bulk polymerized material for PVC-U applications (unplasticized PVC), and solution polymerization for applications such as surface coatings where the PVC (usually as a copolymer) is used in solution form [4].

PVC is produced in two general forms: rigid (known as PVC-U) and flexible. Virgin PVC is not a very useful resin. Various additives are generally compounded into PVC to give the material a diverse range of properties from rigid to flexible. Additives can influence products properties: mechanical properties, color, clarity, weather resistance, etc. A PVC compound may contain the following ingredients: heat stabilizers, plasticizers (in case of flexible PVC), extenders, lubricants, fillers, pigments, processing aids, impact modifiers, fire retardants, UV stabilizers, mineral fillers, optical bleaches, biocides, antistatic agents, blowing agents, and viscosity modifiers [3,4,7,8].

17.2.3 Production of the poly(vinyl chloride) films/foils/plate

Before making a 3D model with sheet lamination process, the material in this case PVC must meet the requirements of the SHL process, like good connection between laminated layers and no chemical reaction between PVC and adhesion material [9].

For sheet lamination process material must be in the form of films, foils, or plate. PVC is produced for the SHL process by calendering and most often by extrusion. Extrusion is a process of continuous primary shaping by

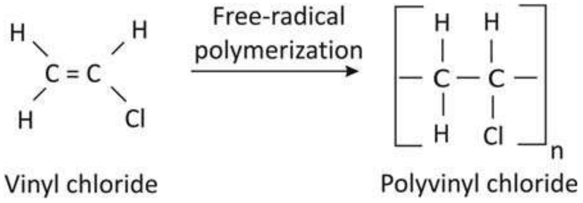

FIGURE 17.1 Synthesis of poly(vinyl chloride) (PVC) [6]. *Reprinted from [6], Copyright (2019).*

pushing a liquid polymer through a nozzle. The extruded polymer hardens into the product by gelling and/or cooling, or by polymerization and/or cross-linking and drying. The product is stacked or rolled up. Two product measurements are controlled, width and thickness, or in the case of a circular cross section one (diameter). Extrusion produces endless products or semifinished products, e.g., pipes, rods, films, foils, and plates, other solid and hollow profiles, fibers, insulation or sheaths of cables, or coated substrates [10]. Flat die nozzles are used for the production of PVC films, foils, and plates. For sheet lamination PVC foil is made in thickness of 0.168 mm [11].

17.2.4 PVC in the sheet lamination

This material makes products immune to certain problems, that have, for example, paper; it is not necessary to use lacquer to prevent moisture absorption, PVC foils can be produced in different colors (blue, red, black, amber, etc.) so it is not necessary to paint finished product [11]. But only a monochrome product composed of several parts of different colors can be obtained; however, this requires changing the roll of foil of different colors in a 3D printer.

The production of PVC in the sheet lamination process requires the application of a proprietary water-based adhesive. Since no extra heating is required during PVC production, in the event of a power failure, production can continue on the layer on which it stopped, without reducing the mechanical properties of the product [11].

When making PVC, there is no need for special preparation of the material, equipment (3D printer), and postprocessing, except for decubing from excess material that served as a supporting structure. Due to the step-stair effect, postpolishing on PVC products is possible. The biggest disadvantage is the large amount of waste, but PVC is a material that can be easily recycled by responsible collection and separation from other types of polymer materials.

17.2.5 Properties of PVC made by sheet lamination

According to the method of production in additive manufacturing and SHL (explained in Chapter 11), the properties of the material depend on the product orientation in the machine building chamber.

In the field of additive manufacturing in all processes there are many parameters that affect the properties of the product, such as product orientation on the build plate, speed, energy density, raster, layer thickness, build plate temperature and manufacturing temperature, etc., but in the process SHL of all these parameters it is only possible to adjust the orientation of the product on the build plate because, for example, the thickness of the layer depends on the thickness of the PVC foil and as described in Chapter 11 no other parameter exists [12,13].

Test specimens for testing the properties of PVC product was made on 3D printer *SD 300 Pro* from company *Solido Ltd.* Figs. 17.4–17.7 are the results of dimension deviation, roughness, and mechanical testing (tensile and flexural properties) of PVC with respect to three different orientations according to Fig. 17.2 (Lxy – test specimen laid in xy plane with height in z direction 4 mm; Pxy – test specimen raised in xy plane with height in z direction 10 mm; Pz – test specimen raised in z-axis with height 75 mm and 80 mm depending on whether the specimen is for tensile or

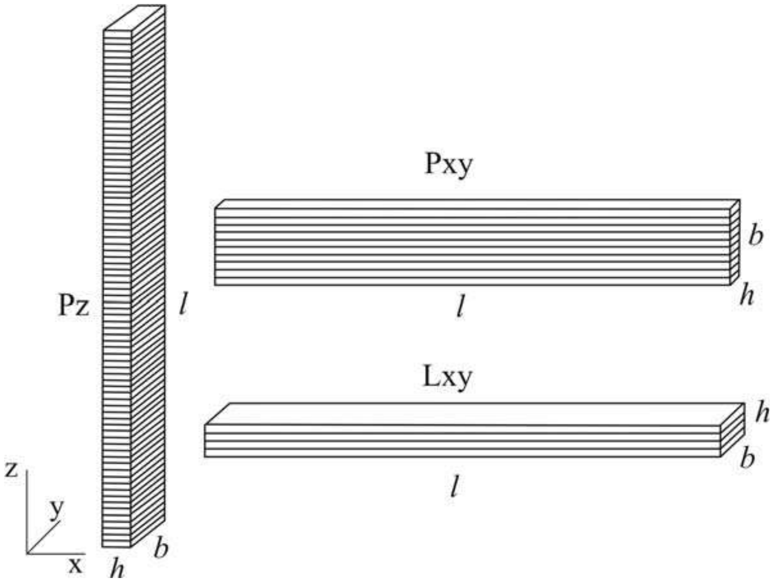

FIGURE 17.2 Orientation of layer in working chamber [12]. *Reprinted from Technical Gazette [12], Copyright (2011), with permission from Technical Gazette.*

flexural tests). The tensile properties are tested according to ISO 527:2012 and the flexural properties according to ISO 178:2011 standard. The test was carried out on universal testing machine *Messphysik Beta 50-5* (*Messphysik Materials testing GmbH*, Fürstenfeld, Austria), with a maximum loading force of 50 kN at a speed of 5 mm/min at a temperature of 23°C. For tensile properties the 75 mm long specimens were made since the working chamber is of maximum height of 135 mm so that it is not possible to make higher test specimens in z direction. For testing surface roughness *Mahr Perthometer S8P*, serial number 0265 is used. Measurements have been carried out with the external guided probe FRW = 750, with probe needle radius of 10 μm and probe needle angle 90°. The important machine data are marginal value of the GS electrical filter (marginal wavelength for roughness profile) $\lambda_c = 0.8$ mm and reference length $L_t = 5.6$ mm [12].

Fig. 17.3 shows the test specimen for mechanical testing made by the SHL procedure with PVC material.

Deviation from nominal values is in the range that is defined by standard (±0.2 mm) in all three orientations what can be seen in Fig. 17.4. The smallest deviations have the orientation Lxy. It is, however, interesting that in Pz orientation the highest deviations are in x-axis, i.e., thickness *h*, and in Pxy orientation in z-axis, i.e., width *b*, whereas Lxy orientation has by far the least deviations. Such deviations in z-axis are consequences of the very thickness of PVC film of 0.168 mm and glue between the layers [12].

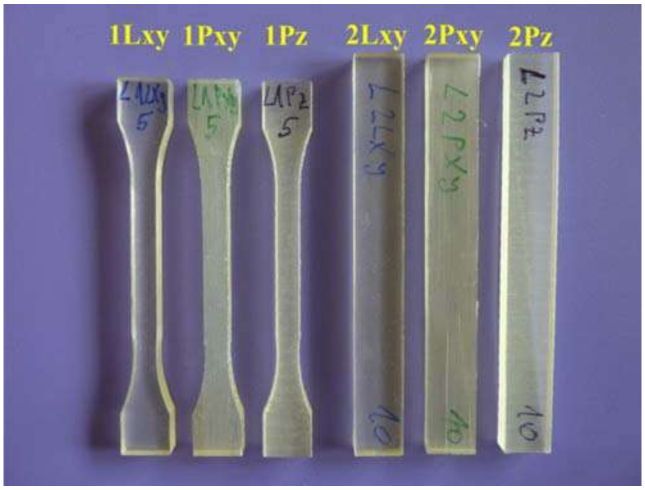

FIGURE 17.3 PVC test specimens made by SHL process [12]. *Reprinted from Technical Gazette [12], Copyright (2011), with permission from Technical Gazette.*

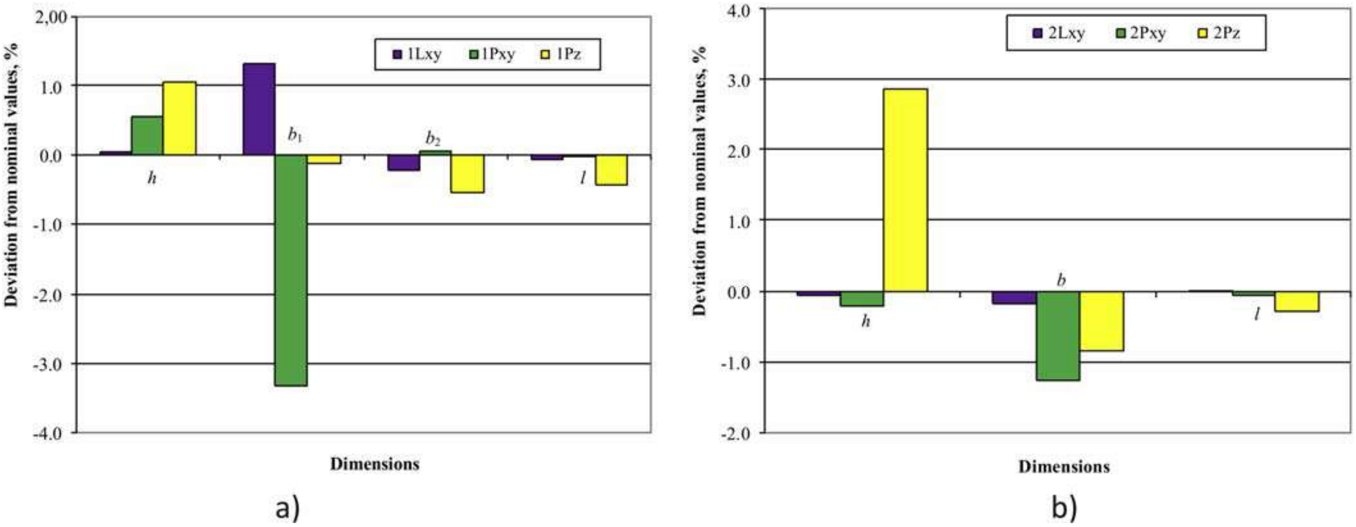

FIGURE 17.4 Deviation from nominal values: (A) tensile test specimen, (B) flexural test specimen [12]. *Reprinted from Technical Gazette [12], Copyright (2011), with permission from Technical Gazette.*

SHL procedure provides low surface roughness parameters in all three orientations. However, the lowest are in Lxy orientation (arithmetic mean $\overline{x} \pm$ SD of the mean arithmetic deviation of profile; Lxy: $R_a = 0.03 \pm 0$ μm, Pxy: $R_a = 2.86 \pm 0.83$ μm, and Pz: $R_a = 3.36 \pm 0.26$ μm) which is only logical since the final layer is pure PVC film, independent of the production method (lamination method). Accordingly, roughness in orientation Pxy and Pz is 95 times greater than in Lxy orientation (Fig. 17.5) [12].

The specimens of Lxy orientation have the highest strain, even up to an average of $\varepsilon_p = 207 \pm 45\%$, whereas the test specimens of Pz orientation have only $\varepsilon_p = 24 \pm 2.6\%$, which is 8.5 times lower value. Although the differences are very small, it is interesting to note that the highest tensile strength is not for test specimens of Lxy orientation (22 ± 0.7 MPa), but the test specimens of Pxy orientation (24.5 ± 1 MPa). Orientation does not affect the tensile modulus (Fig. 17.6) [12]. All tensile properties were measured on the universal testing machine and calculated according to equations in the HRN EN ISO 527:2012 standard.

The diagram in Fig. 17.7 shows that the least favorable position, i.e., the one with the lowest flexural properties, is the Pz orientation, while Pxy has somewhat lower properties than Lxy orientation, except for the flexural modulus [12].

The flexural properties show an identical thing like tensile properties for the orientation Pz whose flexural strength and flexural modulus are twice less than in the case of the other two orientations (Fig. 17.7) (Pz $\sigma_{\mathrm{fM}} = 14.2 \pm 0.7$ MPa, $E_f = 0.5 \pm 0.1$ GPa, Lxy $\sigma_{\mathrm{fM}} = 32.9 \pm 1.1$ MPa, $E_f = 1.1 \pm 0.1$ GPa; Pxy $\sigma_{\mathrm{fM}} = 31.3 \pm 0.9$ MPa, $E_f = 1.2 \pm 0.02$ GPa) [12]. All flexural properties were measured on the universal testing machine and calculated according to equations in the HRN EN ISO 178:2011 standard.

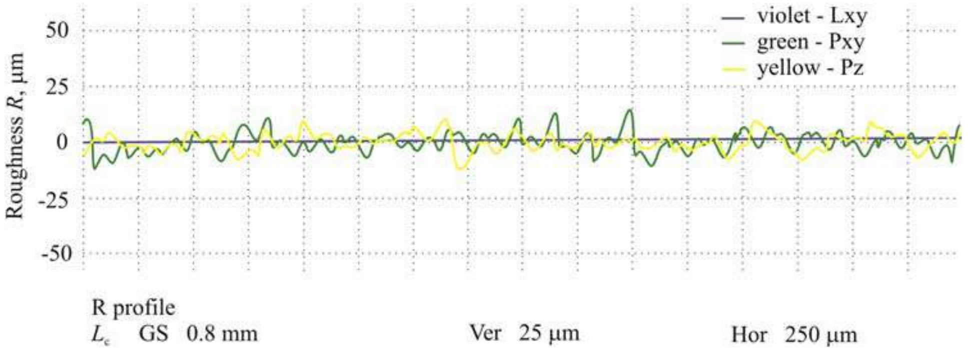

FIGURE 17.5 Surface roughness of PVC [12]. *Reprinted from Technical Gazette [12], Copyright (2011), with permission from Technical Gazette.*

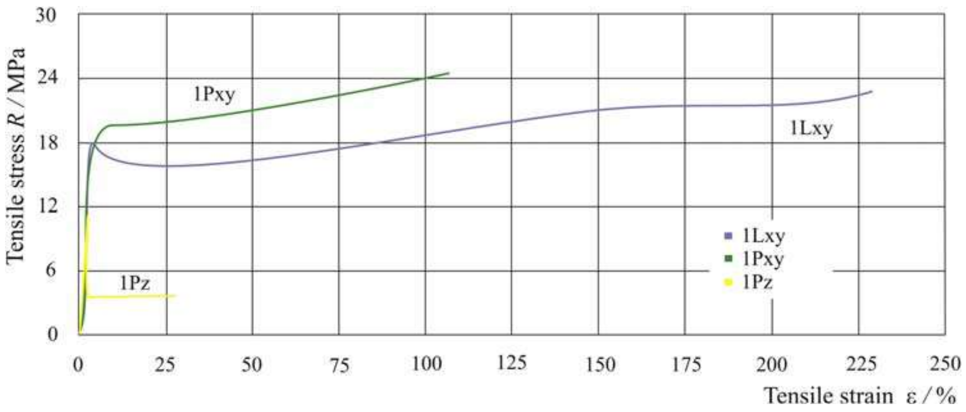

FIGURE 17.6 Diagram of tensile stress–strain for PVC [12]. *Reprinted from Technical Gazette [12], Copyright (2011), with permission from Technical Gazette.*

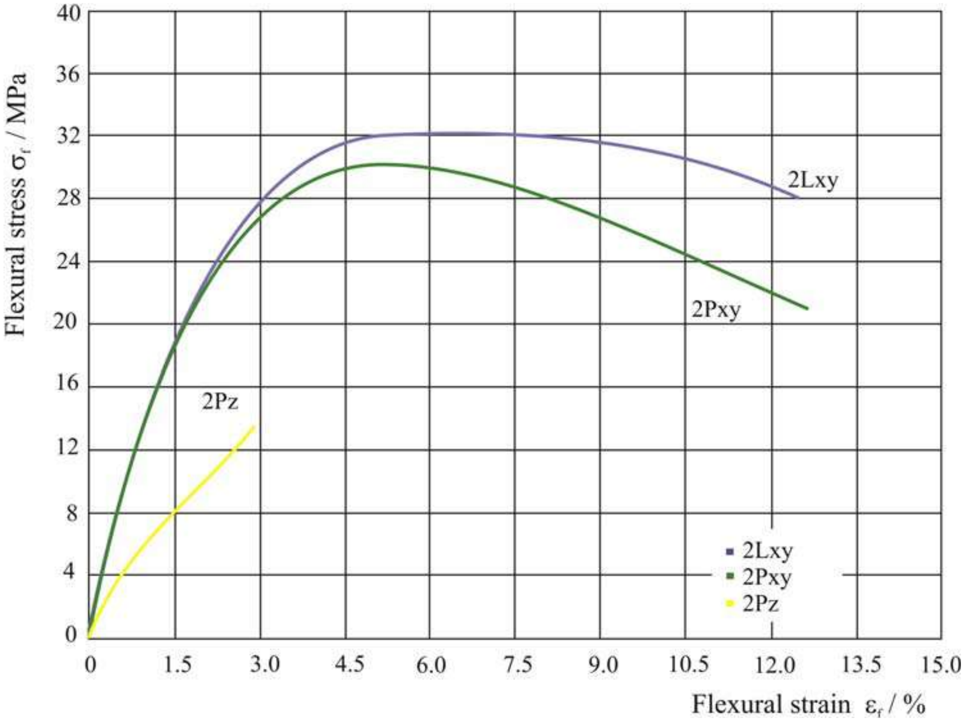

FIGURE 17.7 Diagram of flexural stress–strain for PVC [12]. *Reprinted from Technical Gazette [12], Copyright (2011), with permission from Technical Gazette.*

17.2.6 Application of PVC made by sheet lamination

PVC material in sheet lamination process can be used in different industries like other materials and other additive processes. PVC is inexpensive material with good mechanical properties, but limitation of the sheet lamination process led application of PVC to test form, fit and assembly (i.e., ability to quickly produce and test models for snap-fit and assembly in-house, multiple parts can be printed with PVC and assembled together to provide a physical representation of some design), visualization, concept verification for the final stage of product development, ergonomic studies (model can be tested for size, weight, strength and shape because PVC is durable, flexible material with smooth surface), functional presentations and production of the molds for small batch via injection molding or injection silicon-based materials [11,13,14] (Fig. 17.8).

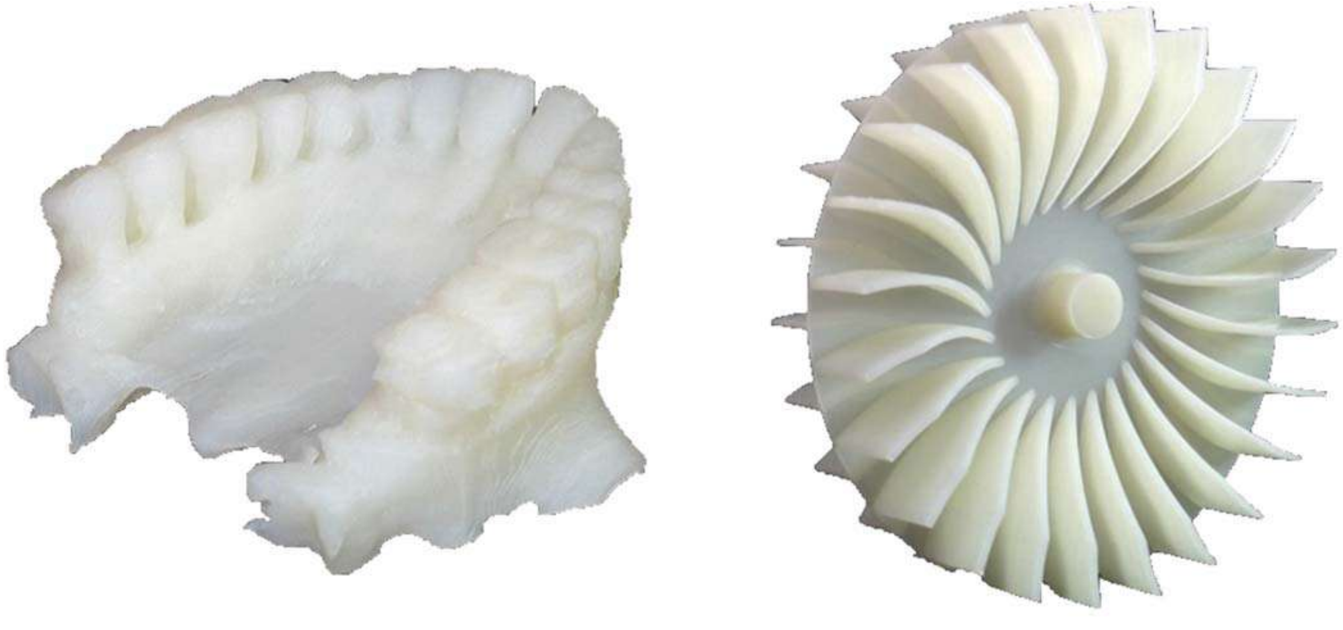

FIGURE 17.8 Visualization and concept models made with PVC [Foto: A. Pilipović, Euromold 2011].

17.3 Polymer composites

17.3.1 Introduction to polymer prepregs

Prepregs are usually made of epoxy and phenolic resins and reinforcements, but fillers and other additives are not added to them. After soaking with resin, the fabric passes through rollers where the excess resin is separated and passes through a furnace where the solvents evaporate and the first hardening phase occurs. The prepreg is then cooled to prevent further solidification that will be achieved when making the final product with the SHL process [15].

Since prepreg is a preprepared material with matrix, it is easy to work with it because it does not require mixing the matrix with the catalyst, as is the case with hand layup lamination. Another great advantage of prepregs in SHL process is the use of various types of reinforcements (glass, carbon, aramid, etc.) and matrices (thermoplastics like polyamide (PA 6, PA 6.10, PA 4.1, PA 11, PA 12), poly(ether etherketone) (PEEK), poly(ether ketoneketone) (PEKK), poly(ether imide) (PEI), poly(phenylene sulfide) (PPS), polypropylene (PP), polyethylene (PE), poly(ethylene terephthalate) (PET), poly(ether sulfone) (PES), and polycarbonate (PC)) [15,16].

17.3.2 Polymer composites in the sheet lamination

The application of polymer composites in the SHL process began in the 1990s. Thus, the authors Klosterman et al. explored their application in the work structural composites via SHL and found that complex shaped parts can be made from range of composite prepregs similar to paper SDL production. However, due to the transient temperature and pressure application associated with the SHL process, a secondary postprocessing is required for final part solidification and curing. Without the postcure, the functionality of composite parts is severely reduced. In that form parts cannot be used for tooling applications [17].

Klosterman et al. investigated two prepreg systems, both epoxy and glass fiber. They found that the preparation of the prepreg plays a major role in the process itself and whether there will be places left with uncured resin or the layers of the prepreg will be glued to the heated roller that passes over each new layer and cross-links it [17,18]. At that time, the improvement of the properties of the products obtained by the SHL process was in the application of composites, but many more improvements were needed in the machines themselves, which would lead to greater application of polymer fiber composites (prepregs) in SHL process. These improvements include automations of layup lamination and curing of resin inside of prepreg [17].

After that, additive manufacturing of continuous fiber-reinforced thermoplastic composites was under development, especially with fused deposition modeling (FDM). However, weak interlayer bonding voids between layers and low volume ration of fibers suppress the application of these systems (prepregs and additive manufacturing) in, for example, aerospace and defense industry [18].

So authors Parandoush et al. introduced new approach of SHL prepreg composite sheets (thermoplastics reinforced by carbon fibers). First step in the process is cutting the prepreg sheets based on the sliced CAD geometry, and then bonding layer upon layer using a CO_2 laser beam and a consolidation roller system (Fig. 17.9A, B, and C). High temperature above the resin melting point from the laser irradiation and pressure from the consolidation roller causes full consolidation of the prepreg layers (Fig. 17.9D and E). Moreover, the proposed technique also enables controlling the alignment of carbon fiber in printed layers. CFRTPs with unidirectional 0°, cross-ply $0/90°$, and $0/-45/0/45°$ fiber reinforcement can be produced and the proposed 3D printing method is broadly beneficial for industries requiring high performance and lightweight structural materials with complex geometries [19,20].

The specifics in *EnvisionTEC* 3D printer is that polymer prepreg roll must be preheated and waxlike substance must be applied in crosshatch areas where no lamination is desired. Second heating, heated pressure roller insures full impregnation of layers of prepregs. Postprocessing (decubing) is necessary for separation of excess material that served as a supporting structure in the same way as in the manufacture of products with PVC (crosshatch areas are easily removed because they are not stuck together because of the waxlike substance). Resulted parts are not near-shaped products but instead it is very accurate finished goods with properties equivalent to or better than those from hand layup [21].

A special feature of 3D printer is that the whole build area sits on a table which can be rotated in clockwise or counterclockwise directions [21] in the middle of the manufacturing process (before placing the next layer of prepreg on the previous layer), thus achieving different orientation of individual layers (i.e., it is possible to build a customized layup sequence), which contributes to product properties and thus their application in various industries [21].

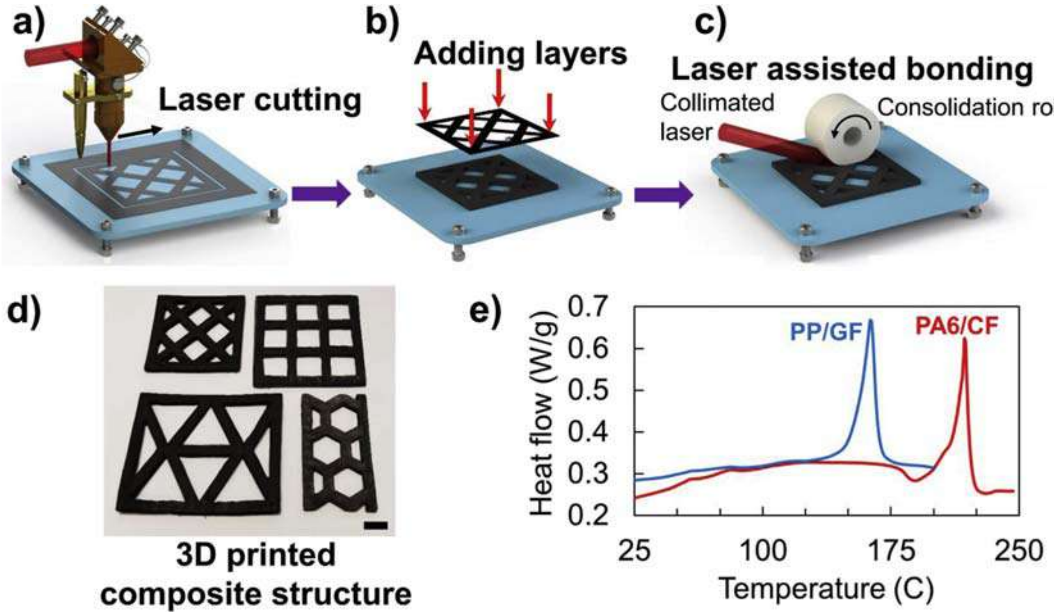

FIGURE 17.9 Schematic illustration of 3D printing lamination process of the carbon fiber-reinforced thermoplastic composites: (A, B, C) process, (D) printed examples, (E) DSC curves of polyamide 6 (PA 6)/CF and polypropylene (PP)/GF prepreg composite sheets [19]. *Reprinted from [19], Copyright (2018), with permission from John Wiley and Sons.*

17.3.3 Properties of polymer prepregs made by sheet lamination

Parandoush et al. found that the void content is low by computed tomography scans and interlaminar bonding strength is as high as conventional autoclave method by lap shear strength tests. The excellent interfacial bonding strength and high volume ratio of continuous carbon fiber contribute to the highest reported tensile strength (668.3 MPa) and flexural strength (591.16 MPa), for all 3D printed CFRTPs [19] (Fig. 17.10A and B).

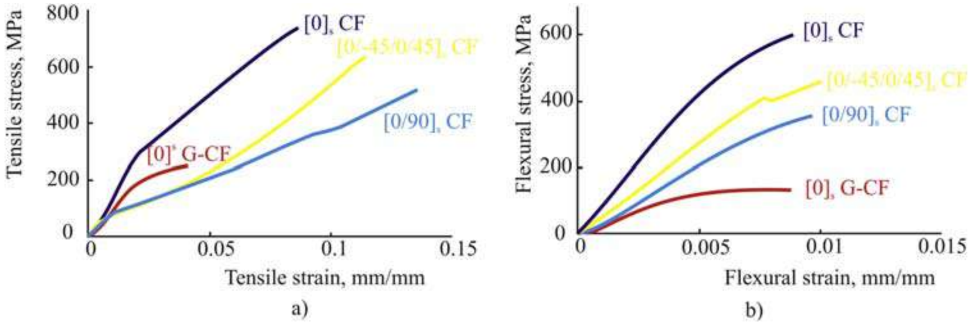

FIGURE 17.10 Properties of SHL prepregs: (A) tensile properties, (B) flexural properties [19]. *Reprinted from [19], Copyright (2018), with permission from John Wiley and Sons.*

17.3.4 Application of prepregs

Composites can be tailored for exceptional toughness, environmental resistance, vibration dampening, low flammability characteristics, high wear resistance, and high strength to weight ratio. Composite 3D parts have incredible strength to weight ratios that enable applications never before possible [22].

With thermoplastics and fibers (composite prepregs) it is possible to directly manufacture functional high-quality lightweight technical components for aerospace and automotive industries, consumer and sports goods, and

FIGURE 17.11 Product made with carbon fiber and PEEK [16]. (Source: *courtesy of EnvisionTEC GmbH).*

medical devices [22]. Application of polymer prepreg (PEEK reinforced with carbon fiber) in sheet lamination process is shown in Fig. 17.11.

17.4 Environmental impact with the respect to materials and SHL process

Nowadays, environmental protection and proper disposal of waste generated in production is very important. In additive manufacturing processes, as stated by the authors M.R. Khosravani and T. Reinicke, it is important to consider three aspects: energy consumption, waste management, and air pollution [23].

For energy consumption it can be concluded as for other AM processes, i.e., energy consumption is affected by processing parameters (different materials required different heat, that is, with increasing processing temperature energy consumption increases, also energy consumption increases if the speed is lower and the layer thickness is thinner and the resolution is better) [23]. When looking at the effect of temperature on PVC processing it is not as with other AM processes because no heat is developed when gluing layers of PVC foils, but the application of polymer composites requires a temperature for the matrix to harden completely, and the temperature value depends on the type of thermoplastic in the prepreg. Furthermore, in the processing of PVC and prepregs there is no possibility to adjust the thickness of the layer, nor the resolution so that the energy consumption is always the same. The speed can possibly be increased, but it has a big impact on delamination if it is too high. It should also be added that the preparation of polymer materials in the form (foil, sheet, prepreg) in which it enters the SHL process consumes energy.

Furthermore, the authors in Ref. [23] conclude that material waste management in 3D printing can be classified into two categories: (1) using recycled materials in 3D printers, and (2) recycling waste materials produced in 3D printing processes. Both of these activities can significantly reduce the overall environmental impact of AM.

Waste is a big topic not only for additive manufacturing processes, nor for SHL processes but for the whole production. Currently, polymer materials have a very negative impact on the human population, which is mostly contributed by inaccurate inscriptions on various popular magazines, portals, and networks. But polymeric materials if well and properly disposed of (collected and separated) have great potential for recycling. Whether it is mechanical, chemical, or energy recovery. This is also the case with PVC, but also with prepregs used in the SHL process, primarily because only prepregs with a thermoplastic matrix are used in SHL process. But in the case of mechanical and chemical recycling, the question arises as to where such recycled material could be reused, whether again in the SHL process or in some classic production. Thus, energy recovery must not be discarded, especially in the case of SHL processing of composite prepreg, because it may not be economical worthwhile to separate these two components (thermoplastics matrix and fiber reinforcement).

When it comes to air pollution, the processing and recycling of PVC and composites in the SHL process should definitely be linked. Special separation and recycling should be introduced for both types of materials, but the question of cost-effectiveness arises. Although perhaps at some point SHL was exclusively processed with PVC, the waste quantities after cutting the excess foil were not enough to collect, recycle, and reuse them. Also since SLCOM 3D printers are currently expensive, there are also small amounts of waste that are generated in this process. But every individuals, small or large company, should organize the separation of excess material (scrap or waste) in production, which will certainly affect the management of waste and air pollutants.

17.5 Conclusion

Many advantages of PVC, such as compatibility with many different kind of additives and adhesives, easy production in the form of the films/foils/plate by conventional extrusion process, and good mechanical properties, make it an excellent material for application in the SHL process. Regarding the obtained results of mechanical properties and dimensions, it can be concluded that the orientation of the product on the build plate of the 3D printer has a great influence. The orientation in the *z*-axis has the lowest mechanical properties, so it is necessary to know in which direction the load will be on finished product before processing. As with any other processing by additive manufacturing with any material, whether PVC or polymer prepreg, it is necessary to determine whether rapid production, mechanical properties (which entails the choice of material and then the additive manufacturing process), dimensional stability, and finally the price to get the optimal product.

However, the sheet lamination has not developed in the last few years in the field of processing of polymer materials. Probably the reason is that the only material available was PVC. This was good while additive manufacturing was applied exclusively to prototyping, but nowadays additive manufacturing is applied to functional products with good properties. As much as PVC has good mechanical properties and products made of PVC with SHL process show good lamination adhesion and dimensional stability, other polymer materials have been required and production and the development of PVC with SHL process has stopped.

Along with numerous developments of the 3D SHL printers, materials were also developed in the form of the sheets, primarily metals and ceramics, but also polymer composites. For polymer composites, because of the sheet, basic form of materials that can enter a 3D printer, the development went only to the application of prepregs, i.e., already prepared fiber material with pre-cross-linked resin. So far, only thermoplastics prepregs, i.e., polyamide (PA 6, PA 6.10, PA 4.1, PA 11, PA 12), poly(ether etherketone) (PEEK), poly(ether ketoneketone) (PEKK), poly(ether imide) (PEI), poly(phenylene sulfide) (PPS), polypropylene (PP), polyethylene (PE), poly(ethylene terephthalate) (PET), poly(ether sulfone) (PES), and polycarbonate (PC) reinforced with unidirectional or multidirectional woven glass, carbon, aramid, and poly(oxy benzimidazole) (PBO) fibers are used. In the future composite prepregs with sheet lamination could offer an alternative to hand layup parts and may even use thermosets.

With the arrival of the prepregs 3D printer on the market even greater possibilities in the application of polymer composites in the SHL process open up, but the 3D printers for production of composites are not cheap, so only the future will show the new developments of the materials for the SHL process.

References

[1] Creative Mechanisms Staff, Everything You Need about PVC Plastic, 2016. https://www.creativemechanisms.com/blog/everything-you-need-to-know-about-pvc-plastic (Accessed 01 May 2020).
[2] Polymer Properties Database, Polyvinyl films, 2015—2020, http://polymerdatabase.com/Films/PVC.html (Accessed 01 May 2020).
[3] V.R. Sastri, Plastics in Medical Devices, Properties, Requirements and Applications, first ed., Elsevier, 2010 https://doi.org/10.1016/B978-0-8155-2027-6.10006-6 (Chapter 6 - Commodity Thermoplastics: Polyvinyl Chloride, Polyolefins, and Polystyrene), 73—119, ISBN: 978-0-8155-2027-6.
[4] M. Gilbert (Ed.), Brydson's Plastic Materials, eighth ed., Elsevier, 2017 (Chapter 13, M. Gilbert, S. Patrick, Poly(Vinyl Chloride).
[5] S.G. Patrick, Practical Guide to Polyvinyl Chloride, Rapra technology, Shawbury, 2005.
[6] A. Pilipović, Structure and Properties of Polymer Materials, Lectures, University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture, Zagreb, 2019.
[7] British Plastics Federation, Polyvinyl Chloride PVC, https://www.bpf.co.uk/plastipedia/polymers/pvc.aspx (Accessed 05 May 2020).
[8] Teknorapex, How Is PVC Made, Anyway?, 2017, in: https://www.teknorapex.com/the-pvc-production-process (Accessed 05 May 2020).
[9] Manufacturing Guide, Laminated Object Manufacturing, LOM, https://www.manufacturingguide.com/en/laminated-object-manufacturing-lom (Accessed 21 May 2020).
[10] I. Čatić, Production of Polymer Parts, Society of Plasticy and Rubber Engineers, Zagreb, 2006. https://www.bib.irb.hr/266464 (Accessed 20 June 2020).
[11] Buy 3D Printer, Solido 3D Printer Review, http://www.buy3dprinter.org/3d-printer-reviews/solido-3d-printer-review/ (Accessed 01 July 2020).
[12] A. Pilipović, P. Raos, M. Šercer, Experimental testing of quality of polymer parts produced by laminated object manufacturing — LOM, Technical Gazette 18 (2) (2011) 253—260.
[13] Javalin Technologies, Learn how to Print Plastic Models of your SolidWorks Parts, 2010. http://www.javelin-tech.com/newsletter/tech_old/2010/february/video_solido.htm (Accessed 02 July 2020).
[14] Dassault Systèmes, 3D Experience Marketplace, Sheet lamination - LOM, SL, https://make.3dexperience.3ds.com/processes/sheet-lamination (Accessed 02 July 2020).
[15] A. Pilipović, Composite Part Productions — Reinforcement, Lectures, University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture, Zagreb, 2019.
[16] EnvisionTEC, https://envisiontec.com/3d-printers/slcom-1/ (Accessed 02 July 2020).

[17] D.A. Klosterman, R.P. Chartoff, B. Priore, N. Osborne, G. Graves, A. Lightman, S.S. Pak, J. Weaver, Structural composites via laminated object manufacturing (LOM), in: International Solid Freeform Fabrication Symposium, The University of Texas at Austin, 1996, pp. 105–115.

[18] D. Klosterman, R. Chartoff, G. Graves, N. Osborne, B. Priore, Interfacial characteristics of composites fabricated by laminated object manufacturing, Compos. Part A 29A (1998) 1165–1174.

[19] P. Parandoush, C. Zhou, D. Lin, 3D printing of Ultrahigh strength continuous carbon fiber composites, Adv. Eng. Mater. 1800622 (2018) 1–8.

[20] P. Parandoush, Additive Manufacturing of High-Strength Continuous Fiber Reinforced Polymer Composites, Disertation, Kansas State University, Manhattan, KS, 2019, https://krex.k-state.edu/dspace/handle/2097/40236 (Accessed 02 July 2020).

[21] G. Gardiner, Three New 3D Printing Technologies for Composites, 2016. https://www.compositesworld.com/articles/three-new-3d-printing-technologies-for-composites (Accessed 02 July 2020).

[22] 3HTi, Industrial-Scale Printing: SLCOM 1, https://3hti.com/industrial-scale-printing-slcom-1/ (Accessed 02 July 2020).

[23] M. Khosravani, T. Reinicke, On the environmental impacts of 3D printing technology, Appl. Mater. Today 20 (2020) 100689, https://doi.org/10.1016/j.apmt.2020.100689.

CHAPTER

18

Polymers for 3D bioprinting

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18.1 Introduction

Polymers can be processed using different techniques, including solvent casting, hot-melt extrusion, injection molding, and very popular 3D printing methods. The most commonly used 3D bioprinting processes for polymers are fused deposition modeling (FDM), selective laser sintering (SLS), and stereolithography (SLA) [1,2].

3D printing enables the precise transformation layer-by-layer of 3D virtual models created by computer-aided design (CAD) into physical 3D objects. 3D bioprinting is a form of additive manufacturing (AM) used to produce biomaterials from a bioink, often comprising living biological cells, biocompatible polymers and biomolecules for functional tissues and organs, and drug delivery systems [3,4]. 3D bioprinting is a versatile, reproducible, highly adaptable, and very cost-effective fabrication process. It offers a unique opportunity to produce a biomaterial with complicated shapes, desired porosity, pore design, and hence the required mechanical properties, unattainable by conventional methods [5–7]. The precise control over the material characteristics such as physical, chemical, and biological properties (degradability, biocompatibility, mechanical strength, composition, architecture, structure, and other functional properties, e.g., electrical, optical, or thermal) is enabled with the use of 3D printing technique [8].

Object production using 3D techniques includes several steps: computer-aided data acquisition and optimization of the geometry according to printer specification, material selection, the printing of the object, and the surface finishing. In the case of the scaffold, the 3D designs are often based on data obtained by computerized medical imaging equipment such as magnetic resonance imaging (MRI) and computed tomography (CT) scans [2,9,10]. This medical imaging techniques allow the construction of complex geometries with well-defined dimensions as prescribed by CAD [11].

18.2 Properties and requirements for bioprinted polymers

The many properties determine whether a given polymer can be used as a bioink. Fig. 18.1 shows the requirements for these polymers. The essential features of polymer intended for 3D printing are their rheological properties (e.g., viscosity) that determine their printability [2,12,13]. Such a polymer should be produced in a repeatable manner, maintain constant properties, also during sterilization, which is necessary for the implementation of biological tests. 3D-printed polymers intended to use in medicine and pharmacy need to meet a series of strict requirements, considering their biocompatibility, interactions with the local body environment, degradation rate, and mechanical properties [14]. In the case of scaffolds, high cell adhesion to the implant surface, mechanical strength, fatigue, fracture resistance, and compressive stiffness is also required [2].

Degradation products of polymers should be nontoxic to the body. The degradation rate of polymers is related to their molecular weight, crystallinity, structure configuration, chemical composition, water diffusion, hydrophobicity, surface charge, material processing, and stresses. Among polyesters, poly(glycolic acid) (PGA) degrades fastest, then polylactide (PLA), and the longest—polycaprolactone (PCL) [15]. The degradable polymers that are susceptible to hydrolysis of the ester backbone in aqueous environments (e.g., body fluids) include polyesters (PLA,

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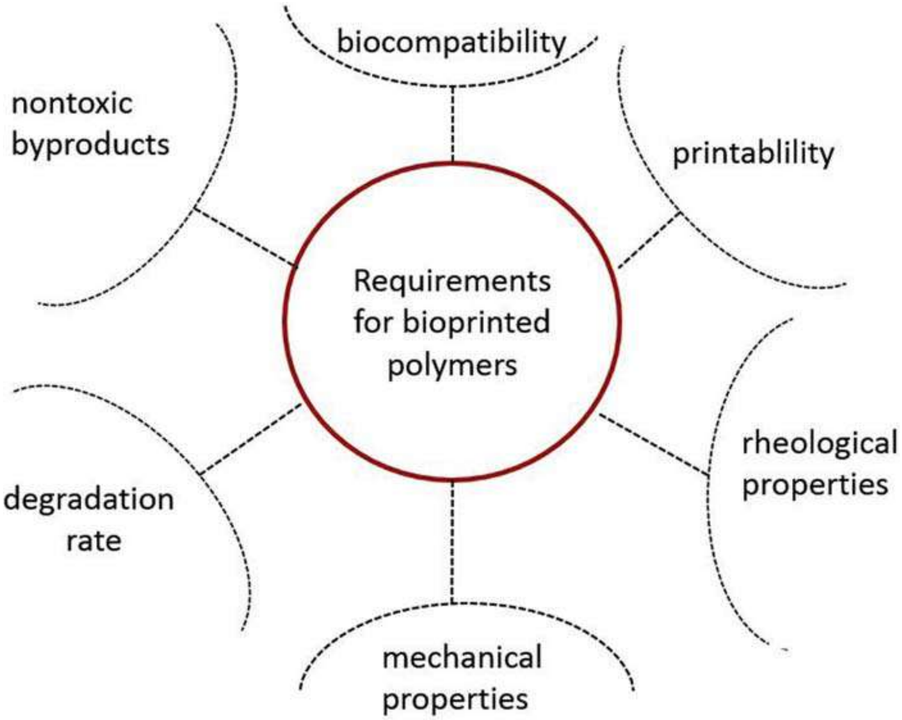


FIGURE 18.1 Requirements for bioprinted polymers [18,19].

polyglycolide, PCL, poly(lactide-co-glycolide) (PLGA), and polyhydroxyalkanoates), polyanhydrides, polycarbonates, polyamides, polyurethanes, and polyphosphates. The degradation products are metabolized to CO_2 and H_2O or are excreted via the kidney [16].

Some applications require the polymer to be bioresorbable, i.e., to degrade in a biologically active environment into nontoxic by-products. Resorbable polymer implants should have tissue compatibility and a known time of complete resorption adapted to the function of the implant. The degradation of implants should be controlled in line with the progressive tissue healing process. Too rapid degradation can cause premature loss of mechanical properties and the release of significant amounts of degradation products over a short period, exceeding the body's ability to excrete it, resulting in prolonged inflammation, especially in polymers that degrade to acidic degradation products, e.g., PLA [17].

For particular applications, specific properties are required, which can be obtained by an appropriate selection of polymer ingredients (copolymers or polymer blends). On the other hand, the combination of more than one biomaterial provides better characteristics than any single type of biomaterial, leading to the development of composite polymeric materials. For example, synthetic polymers have mechanical strength, and natural polymers are more favorable for cell attachment, proliferation, and differentiation. Therefore, a blend of these polymers is used to join these properties in one material [12].

Due to their origin, polymers used as bioink are divided into two groups: synthetic and natural polymers. Synthetic polymers, manufactured under controlled conditions, have predictable and reproducible physical and mechanical properties such as Young's modulus and compressive and tensile strength. An additional advantage of synthetically produced biomaterials is controlling their physicochemical properties (e.g., molecular weight, chemical structure). They are generally easy to process into tissue engineering scaffolds. The most common synthetic polymers are: PLA, PCL, poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA), polyurethane (PU), polyvinylpyrrolidone (PVP), and polyhydroxyalkanoates (PHAs) [7,17,20–26]. The most important natural polymers processed by 3D printing technology are chitosan, gelatin, alginate, hyaluronic acid (HA), collagen, and their blends [21,27,28]. Natural bioinks, mainly derived from an animal source (gelatin, collagen, hyaluronic acid), enhance biological features of biomaterials, facilitate cell attachment and maintenance of differentiation, but they have high batch-to-batch variation, low mechanical stability, and the potential risk of pathogen transfer from the originating organism [29].

The 3D biopolymers are very often printed in the form of hydrogels. Successes have been achieved in designing, e.g., alginate- and gelatin-based ink formulations [28,30–32]. Hydrogels are very attractive for soft tissue regeneration because of the similarity of mechanical properties and organism-environment. Hydrogel networks facilitate cell migration and cell adhesion in bioink that are required for the development of functional tissues [8].

18.3 Applications

The dynamic growth of polymers application in medicine and pharmacy has been observed since the 1960s. In 2010s, 3D printing has offered significant advantages in this field due to the ability to fabricate biomedical and pharmaceutical products with complicated shapes. The main areas of biomedical applications are scaffolds (bone regeneration) and soft tissue repair (e.g., nose, ear, blood vessels, cartilage, tendons, nerve tissue, or skin) [1,4,11,33]. The mechanical properties of scaffolds, i.e., the porosities, compressive stiffnesses, and yield strengths, should be in the ranges 40%–84%, 2.74–55.95 MPa, and 0.17–5.03 MPa, respectively [1]. Very often, the 3D-printed polymers are expected to support cell colonization, growth, and differentiation. Such 3D-printed complex tissue architecture with a spatiotemporal distribution of bioactive substances (cells, growth factors, and others) allows for better tissue regeneration [34]. The 3D bioprinting allows obtaining artificial skin that could be used for wound treatment and tests of drugs and cosmetics, eliminating the need for animal trials [11,35]. The most commonly used polymeric materials for tissue scaffolds include aliphatic polyesters: PLA, polyglycolide, and PCL, which are bioresorbable and easy to process.

There are also studies regarding 3D-bioprinted specific tissues and organs with living cells (e.g., the liver, skin, heart) [2,9]. The complexity of tissues and organs and the low precision of 3D printing cause problems with accurate mapping [2]. There are also issues connected with the vascularization of printed structures [12].

The most important 3D-printed pharmaceutical products are drug delivery systems and wound dressing [12,34,36]. The appropriate selection of a polymer and geometry of the structure enables control of drug release kinetics because the main driving force for drug release is the degradation rate of the polymer matrix [1,11]. The drug delivery system should release its content with precise concentration, distribution, and duration to maintain the therapeutic effect. This technology allows dosage forms to be precisely printed in various shapes, sizes, and textures that are difficult to produce using traditional techniques [7,37,38]. The size and shape (pore size and pore gradients) of the construct have influence on the degradation rate, tissue formation, and vascularization. Drug structure could be customized for an individual patient [14]. In 2015, the first 3D-printed drug was registered and approved by FDA. It was SPRITAM, an antiepilepsy drug, with Levetiracetam as a drug substance [39]. Despite this success, the large-scale production of 3D-printed drugs might be a long way from now [37]. The major obstacles to the rapid development of printed pharmaceuticals are the long processing time and the drug's lack of resistance to exposure times at the high temperatures at which the drug is processed [40]. The latter can break down the drug. The most commonly used polymers in drug delivery systems are PEG, polyvinyl alcohol, and PCL (Table 18.1).

Researchers have also elaborated a new type of wound dressings produced with the use of 3D printing. This method enables the formation of many wound dressings, including biodegradable composite materials, cell-laden, and drug-eluting wound dressings. The use of additive manufacturing allows obtaining a wound dressing with a desired shape as well as properties and facilities the better dressing placement at the wound bed. The most printed polymers as a wound dressing are alginate and carboxymethyl cellulose which is nontoxic and allows good gelation control under mild conditions [41,42].

TABLE 18.1 Examples of 3D-printed polymeric drug delivery systems.

Polymer material	Drug delivered	Implant type	3D printing method	References
Polyethylene glycol	4-Aminosalicylic acid paracetamol	Oral	SLA	[43]
Polyvinyl alcohol	Aripiprazole	Orodispersible	FDM	[44]
Polyethylene glycol	Nifedipine	Oral	Extrusion	[23]
Polyvinyl alcohol	Paracetamol	Oral	FDM	[45]
Polyvinyl alcohol	Prednisolone	Oral	FDM	[46]
Polycaprolactone	Indomethacin	Intrauterine system	FDM	[47]

18.4 Polymers for 3D bioprinting

18.4.1 Polylactide

18.4.1.1 Development

Polylactide (Polylactic acid, PLA) is a biodegradable polymer that can be produced from lactic acid (LA) or renewable sources. PLA is a mass-produced polymer mainly because of the best availability and the most attractive cost of raw materials. It is mainly used in medicine and food packagings for replacing nondegradable polymers such as polyethylene terephthalate and polystyrene. Currently, the large-scale production of PLA is being held by NatureWorks LLC, which is the only industrial manufacturer of large quantities of PLA [48–50].

18.4.1.2 Chemical structure and synthesis

PLA is a thermoplastic polyester with a structure presented in Fig. 18.2. PLA is a chiral polymer obtained from optical isomers: L-lactide, D-lactide, and DL-lactide, and because of that, PLA occurs in the form of PLLA, PDLA, and PDLLA. PLLA and PDLA are semicrystalline polymers due to the stereoregularity of the polymer chain. In turn, PDLLA is amorphous because of its irregular structure [49].

PLA is produced from LA, which can be produced chemically or by bacterial fermentation of sugars from carbohydrate sources such as sugarcane, starch, corn, potato, or tapioca. 70–90% of LA worldwide production is manufactured by fermentation.

PLA can be produced by the polycondensation of LA or by ring-opening polymerization (ROP) of the lactide (the cyclic dimer of LA) (Fig. 18.3). In the polycondensation method, the obtained PLA has a lower molecular weight. In turn, the ring-opening polymerization allows to obtain the high-molecular-weight PLA and to control the PLA properties by adjusting the ratios and the sequence of L- and D-lactic acid units. The ring-opening polymerization route is the most commercial method of PLA production. It consists of a two-step reaction that often involves additional purification steps and generates high costs. The second step reaction is catalyzed by an Sn(II)-based catalyst [49].

18.4.1.3 Characteristics

Many properties of PLA depend on the polymer molecular weight as well as the ratio and the sequence of D- and L-enantiomers in the polymer [49,51]. The essential characteristics influenced by polymer structure are crystallization, crystallinity degree, mechanical and thermal properties (degradation behavior, melting temperature (T_m), or glass transition temperature (T_g)). PLA with PLLA content higher than 90% is semicrystalline with the highest T_m and amorphous with lower T_m in the case of lower than 85%–88% PLLA content. The mechanical properties of polymers are connected with their melting temperature. T_m of enantiomer PLLA and PDLA is ~50°C higher than T_m of single PLLA and PDLA, so enantiomers have better mechanical characteristics, including tensile strength, tensile modulus, and percent elongation to break.

PLA is a biodegradable polymer whose degradation rate is related to its degree of crystallinity. The degradation of this polymer takes place through hydrolysis, which is influenced, among others, by diffusion in the amorphous phase. PLA has good biocompatibility, biodegradability, low toxicity, and good mechanical strength [52]. These properties allow using this polymer as a biomaterial.

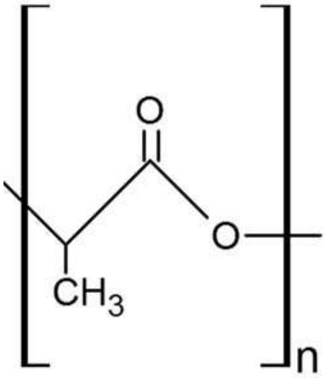


FIGURE 18.2 Chemical structure of PLA.

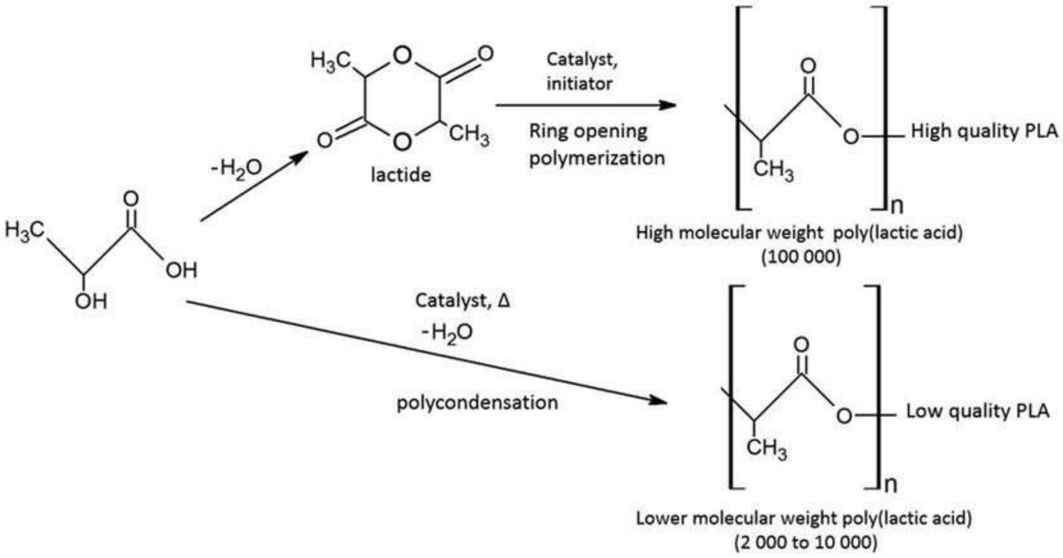


FIGURE 18.3 Manufacturing routes for polylactide.

On the other hand, the use of this pure polymer as a biomaterial is problematic because the biodegradation rate of PLA is too low to match the tissue regeneration process after implantation. Furthermore, the acidic degradation products of PLLA, such as LA, tend to cause aseptic inflammation in tissue [53]. The fact that the surface of PLA is strongly hydrophobic also limits its medical application. Various surface and bulk modifications can be done, such as preparing blends and copolymers with PEG to improve its hydrophilicity [54]. Such composition also increases the biocompatibility and softness of biomaterial.

The degradation rate and degradation mechanism of PLA are influenced by many factors: polymer characteristic (e.g., its crystallinity, structure, or molecular weight) and environmental factors such as medium composition, temperature, and pH. Naturally, PLA degrades by the hydrolysis of ester bonds, but generally, there are four main PLA degradation mechanisms: hydrolytic, photodegradative, microbial, and enzymatic [48].

Degradation rate is very important in the case of PLA-based biomaterials. Such biomaterials should have a precisely defined degradation rate which has to be in accordance with the rate of growing tissue. This accurate degradation rate is also required for drug delivery systems, which PLA-based matrices should have an optimal degradation rate and allow to release of the exact amount of drug [48,50].

Compared to other biopolymers, PLA has well-established properties that facilitate its processing [51]. The main properties of PLA are presented in Table 18.2.

TABLE 18.2 The properties of PLA [48].

Properties	PLA	PLLA	PDLA	PDLLA
Crystalline structure	Semicrystalline	Semicrystalline	Crystalline	Amorphous
Melting temperature (°C)	150–162	170–200	120–150	–
Glass transition temperature (°C)	60–65	50–65	50–65	50–60
Density (g/cm^3)	1.2–1.25	1.24–1.30	1.25	1.25–1.27
Tensile strength (MPa)	21–60	15.5–150	15.5–150	27.6–50
Elongation at break (%)	10–100	12–26	20–30	30–35
Elastic modulus (MPa)		4100		
Tensile modulus (GPa)	2.7–16	7–10	7–10	1.5–1.9

18.4.1.4 Processing

PLA is a polymer that can be processed into a broad spectrum of products. Its processing depends on the polymer structural characteristics. The following methods are used to proceed PLA: injection molding, blow molding, hot press molding, foam molding, thermoforming, and electrospinning. Many manufacturing processes (injection molding, single-stage stretch blow molding, film blowing, and melt spinning) use an extruder for plasticizing the polymer melt [55].

In PLA extrusion, the temperature is paramount for achieving high-quality extruded products. The heater is usually set at 200–210°C, which is about 40–50°C above Tm, in order to ensure that all the crystalline phases are melted and to achieve an optimal melt viscosity for processing. During extrusion, PLA can undergo thermal degradation, leading to the formation of lactide and other by-products. The temperature should be controlled very precisely to avoid degradation.

One of the most important PLA processing methods is injection molding, which allows for forming elements with complex shape and high-dimensional precision. Blown film extrusion is not well suited for PLA processing because of the polymer rheology. PLA has relatively low melt strength, resulted from its thermal and hydrolytic degradations [56].

Thermoforming is mainly used for forming packaging products without complicated shapes. This method is used for making PLA cups, lids, or single-use food trays. Electrospinning is a technique that enables producing fibers with a much smaller diameter than those made using conventional methods. Such fibers can be applied as tissue scaffolds, wound dressing, and drug carriers [22].

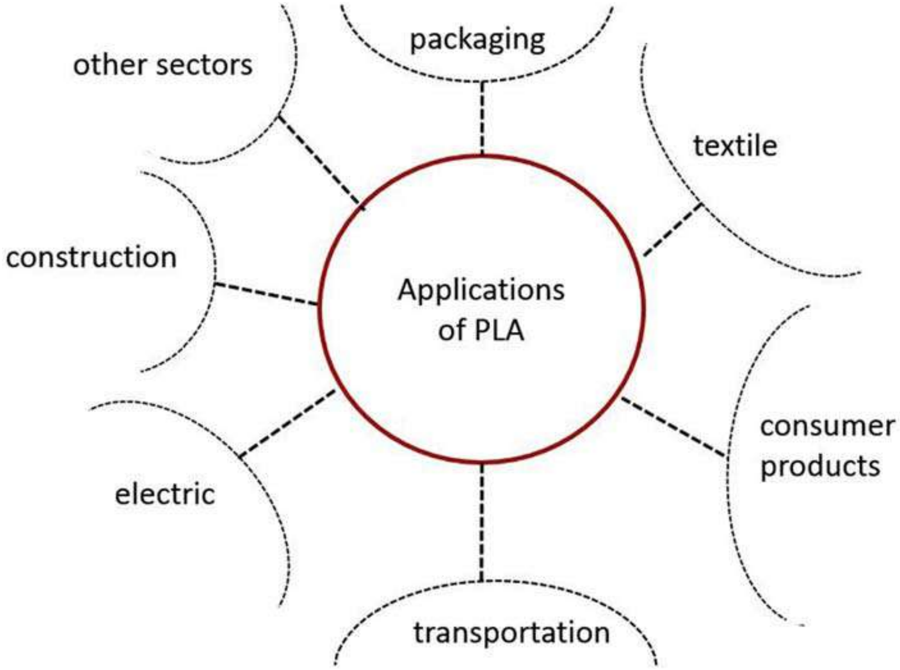
18.4.1.5 Applications

PLA has a wide range of applications starting from packaging obtained from renewable resources to biomedical fields. The typical applications of PLA are shown in Fig. 18.4.

Its properties make it suitable for food packaging applications, particularly cups, bottles, cutlery, containers, and trays. Because this thermoplastic polyester can be spun to form fibers, it is also used as textiles (shirts, furniture textiles) or nonwovens (diapers). PLA is also used as biodegradable mulch films which are used to control the growing conditions of crops and enhance moisture conditions [57].

Medical applications of PLA are related with its similarity in mechanical properties with the natural bone, and they include tissue engineering (e.g., craniofacial bone restoration and cranial defects). It is also used in orthopedic, cardiac, and dental, surgical (stiches), and drug delivery systems applications [48,49,52].

FIGURE 18.4 Applications of PLA.



18.4.1.6 3D printing

PLA is the often used polymer for 3D printing due to its good characteristics, especially their biodegradability and nontoxicity. PLA is easy to print and can be extruded in the temperature exceeding 175°C (Tm). The temperature is mainly held between 190 and 230°C. The extruder doesn't require special hot-end. Vanaei et al. examined the effect of different printing parameters on the sample quality and evaluated the effect of extruder temperature in the FDM process on the PLA fatigue behavior and quality of the 3D-printed parts [58,59].

During printing PLA gives off a sweet aroma which is connected with the source of the polymer. Processed by additive manufacturing PLA is very often used in tissue engineering as biodegradable scaffolds [21,22]. In this case PLA is used with other polymers which reinforce the composite material, e.g., keratin and chitosan, to achieve the precise mechanical and biocompatibility properties [21]. The PLA-based scaffolds are also used as support for the growth of human mesenchymal stem cells (hMSCs). MSCs were seeded on PLA microspheres for bone engineering [60]. The SLA bioprinting was applied to fabricate the PLA-based scaffolds coated with polydopamine for vascularized bone constructs [61].

18.4.2 Polycaprolactone

18.4.2.1 Development

Poly(ε-caprolactone), PCL, was synthesized for the first time from lactone of 6-hydroxycaproic acid in 1934. It has gained acceptance of Food and Drugs Administration and had been used in biomedical fields in 1970s as a long-term drug delivery systems [62]. Due to the slow degradation rate, PCL was soon after replaced by other polymers (PLA and PGA). In the 1990s, PCL was again used in tissue engineering due to its high biocompatibility and ease of processing [63,64]. Currently, the most important producers of PCL are Dow Chemicals, Perstorp, and Polyfea (mainly PCL-based blends) [51].

18.4.2.2 Chemical structure and synthesis

Poly(ε-caprolactone) is an aliphatic polyester composed of hexanoate repeat units (Fig. 18.5). It is a semicrystalline polymer with a degree of crystallinity which can reach 69%.

PCL is synthesized by two main routes: the ROP of ε-caprolactone (a product of the crude oil processing) (Fig. 18.6) and the condensation of 6-hydroxyhexanoic acid. ROP allows to obtain the polymer with higher molecular weight and lower polydispersity and hence, it is more commonly used. In this reaction a various group of catalysts are used: metallic, enzymatic, and organic. Stannous (II) ethylhexanoate is the commonly used catalyst in ROP. Nonetheless, there are a large number of compounds, but at present, metal-based compounds have been studied the most, but enzymatic, organic, and inorganic acids catalysts are becoming more and more popular. Some catalysts need specific conditions to catalyze the ROP of ε-CL, while several can be used in mild conditions. The termination step usually requires the addition of an acid or of an alcohol, but the polymer can also remain alive. The catalyst is

FIGURE 18.5 Chemical structure of PCL.

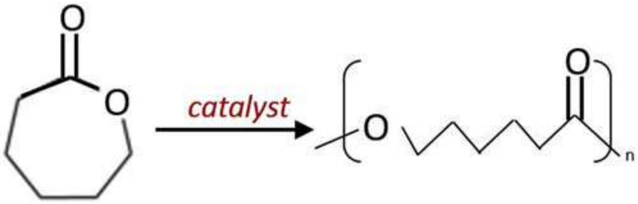


FIGURE 18.6 The synthesis of PCL by ROP of caprolactone.

mainly chosen for the particular application, and the desired reaction conditions [65]. Potentially PCL can also be made from monomers derived from renewable sources.

18.4.2.3 Characteristics

PCL is an important polymer due to its good characteristics: biocompatibility, biodegradability, good bioacceptance, high blend miscibility with a large range of other polymers, and good drug permeability [65]. The majority of PCL properties depends on its molecular weight and its degree of crystallinity. The specific characteristic is shown in Table 18.3.

PCL has good solubility in various solvents such as: chloroform, benzene, toluene, or carbon tetrachloride, and it is slightly soluble in acetone, ethyl acetate, or acetonitrile. Alcohols, petroleum ether, and water don't dissolve PCL. PCL is miscible with many other polymers (PCV, poly(styrene) copolymers, or polycarbonates). PCL is hydrophobic and has low water absorbing capacity. This polymer has relatively high thermal stability and very good rheological properties which allow to process it with a various techniques. The glass transition of PCL is very low and it is in the range from −71 to −55°C. The melting point of PCL is approximately 62°C.

PCL degrades relatively slow within a few months to several years depending on the molecular weight, the crystallinity of the polymer, and the environment. PCL can be completely biodegradable in natural environment by various bacteria. In the first stage, an amorphous phase degrades, which results in an increase in the crystallinity of the polymer. The mechanism of PCL degradation depends on the temperature: at the higher temperatures PCL degrades by end chain scission, and at the lower temperatures by random chain scission.

Mechanical properties of PCL are worse than other polymer biomaterials what limits its medical application. Elongation at break and tensile strength increase along with PCL molecular weight.

18.4.2.4 Processing

Owing to its good characteristic (T_m and rheological properties), PCL is easily processed by conventional melting techniques. PCL-based composites can be produced with reinforced particles or fibers for better mechanical properties. Three different methods are the most popular: solution casting method, melt extrusion technique, and in situ polymerization [66]. Świeszkowski et al. demonstrated that the diameter of 3D-printed PCL fibers with the use of FDM technique has a strong effect on microstructure and mechanical properties of samples [67].

18.4.2.5 Applications

Pure PCL is not so often used because of the poor mechanical properties and the slow degradation rate. In order to widen the usage of PCL, a various PCL-based composites were investigated: PCL copolymers, blends, and PCL−matrix composites [68,69]. PCL is mainly used in tissue engineering as scaffolds and in drug delivery systems (i.e., contraceptives) [70]. Besides the biomedical uses, it is also applicable in microelectronics, and in packaging [65].

Novel approaches of pancreatic islet transplantation have focused on encapsulation of the islets in biomaterial implants which can protect the islets. Vascularization of the implant is a prerequisite for the survival and proper functioning of transplanted pancreatic islets. Scheiner et al. used microspheres based on poly(ε-caprolactone-PEG-ε-caprolactone)-b-poly(L-lactide) copolymers and showed the possibility of the vascularization of this artificial pancreas implants [71].

TABLE 18.3 The properties of PCL.

Properties	PCL
Melting temperature (°C)	56−65
Glass transition temperature (°C)	(−65)−(−60)
Decomposition temperature (°C)	350
Density (g/cm^3)	1.071−1.200
Tensile strength (MPa)	4−785
Elongation at break (%)	20−1000
Young's modulus (GPa)	0.21−0.44
Intrinsic viscosity (cm^3/g)	0.9

18.4.2.6 3D printing

The most common products made of PCL with 3D printing are innovative cell scaffolds for bone tissue regeneration. Different 3D printing techniques are used, e.g., SLS or FDM. Both techniques enable the production complicated scaffold with reproducibility and precise porosity that can be tuned to optimize conditions for cell growth and proliferation. Scaffolds with micropores obtain with the use of SLS that facilitates cell attachments. To improve biocompatibility and improve cell growth, various scaffold geometries were investigated [11]. Ostrowska has found that the best properties of PCL material obtained by FDM, congenial to natural bone, were obtained for a structure with a fiber angle of 60° [17]. Other PCL application as scaffolds was proposed by Yao, who elaborated PCL—hydroxyapatite materials with FDM technology [72]. Kang et al. printed cell-laden hydrogels from PCL. They generated 3D biomaterials loaded with cells with various architectures with the potential to form various vascularized tissue types [73]. There are also attempts to produce highly porous PCL-based scaffold with myoblasts for cardiac tissue engineering by SLS method. In 2012, Xu et al. fabricated a cartilage-like tissue scaffolds made of PCL and chondrocytes suspended in a fibrin—collagen hydrogel with good mechanical properties [74]. Other combination of PCL with hydrogel was proposed by Lee et al. who produced the auricular cartilage and fat tissue of ear with PEG. Chondrocytes and adipocytes were encapsulated in hydrogel to dispense into the cartilage and fat regions, respectively [50]. PCL-based scaffolds with tricalcium phosphate antibacterial agent reduced the inflammation associated with infections after the implantation [20].

In 1996 Sachs and Cima published the first 3D printing drug studies regarding resorbable ingredient release systems with sandwich-type structures (porous poly(ethylene oxide) inside and dense PCL sheets outside) [75]. It was proved that the polymer systems produced by the 3D printing method are able to control the release of the drugs. Currently, scientists modify the geometry of drugs (in the form of tablets or intrauterine systems) using the 3D printing technique in order to increase the availability of the active substance (e.g., indomethacin) [47,76].

Kosik-Kozioł et al. prepared a porous 3D hybrid PCL-based construct composed of three zones of modified biopolymers: alginate reinforced by PLA fibers, alginate and gelatin methacrylate (GelMA) combined with β-tricalcium phosphate particles, and 3D printed (FDM) PCL scaffold. Such construct was prepared to increase the osteochondral tissue regeneration [77].

18.4.3 Poly(ethylene glycol)

18.4.3.1 Development

PEG is a synthetic polymer derived from petroleum. It is one of the most widely used biocompatible polymer for biomedical applications [78,79]. PEG-based drugs have been approved by the FDA for safe use in humans.

18.4.3.2 Chemical structure and synthesis

PEG is a polymer with the subunit C—O—C (Fig. 18.7). This synthetic polyether is called PEO when its molecular weight is above 20,000, otherwise it's named PEG. The synthesis of PEG is done by polymerizing ethylene oxide, the main ingredient in antifreeze, using a ring-opening technique, which allows for PEGs of a range of molecular weights and molecular weight distributions to be constructed. This range in weights is what makes it suitable for several uses.

18.4.3.3 Characteristics and application

PEG is nontoxic, colorless, inert, odorless, and nonvolatile polymer. Due to its biocompatibility and good tolerance it is very often used as biomaterial.

It is highly soluble in water and aqueous media, and some organic solvents (e.g., benzene, carbon tetrachloride, chloroform). The molecular weight of PEG hasn't got great impact on its characteristics. PEG has hydrophilic properties [80].

18.4.3.4 Applications

PEG has been widely used in biomedical applications such as drug delivery systems, biosensing, and tissue engineering. In the case of drug delivery systems, PEG is mainly conjugated with drugs or other materials (PEGylation)

$$H-(O-CH_2-CH_2)_n-OH$$

FIGURE 18.7 Chemical structure of PEG.

to optimize the pharmacokinetic of drug substance [78]. The most common application of PEG in the pharmacy is its use as laxatives (PEG can draw water into the waste matter, providing a laxative effect). PEG is also used in many pharmaceutical and cosmetic ointments and creams. PEG is also used in tissue engineering and drug delivery system in the form of hydrogels and as a precipitant for DNA isolation and cell crystallization. PEG is often used in the chemical and other industries as a binding and dispersing agent. This polymer occurs as preservative.

The synthesis of PEG is made by polymerizing ethylene oxide, the main ingredient in antifreeze, using an RO technique, which allows for PEGs of a range of molecular weights and molecular weight distributions to be constructed. PEG is one of the best biocompatible and most widely used synthetic polymer hydrogels in medicine and biomedicine, approved by the FDA [81].

18.4.4 Other polymers

18.4.4.1 Poly(hydroxymethylglycolide-co-ε-caprolactone)

Poly(hydroxymethylglycolide-co-ε-caprolactone) (PHMGCL) is a functionalized aliphatic polyester based on PCL. It has higher hydrophilicity due to its hydroxyl groups attached to the backbone, resulting in an increase in cell adhesion, proliferation, and differentiation compared to other polymers. This polymer is biodegradable and biocompatible [82]. 3D scaffolds could be obtained by means of fiber deposition (melt plotting). It was shown that PHMGCL 3D scaffolds lost more than 60% of their weight within 3 months after implantation, while pure PCL scaffolds lost no weight in this time. It was also observed vascularization processes of PHMGCL materials while in the case of PCL no such processes were visible [83].

18.4.4.2 Poly(3-hydroxybutyrate)

Poly(3-hydroxybutyrate) (PHB) (Fig. 18.8) is a natural thermoplastic polyester produced by microbes. It has good biocompatibility and biodegradability. PHBV processing by 3D printing can be made without the incorporation of additives unlike the traditional methods [1]. PHB powder could be processed with SLS technology. It has been proved that PHB powder was not altered after being submitted to 32.5 h of SLS processing [84].

18.4.4.3 Poly(dimethylsiloxane)

An example of a polymer that allows the production of multilayered hydrogels loaded with cells on a nonplanar surfaces is poly (dimethylsiloxane). Such biomaterials can be used in the skin wound repair. The technique was tested on a poly(dimethylsiloxane) (PDMS) mold with 3D surface contours as a target substrate. The highly viable proliferation of each cell layer was observed on both planar and nonplanar surfaces [60].

18.4.4.4 Alginates

Alginates are natural polymers consisting of linear copolymers of β-(1−4)-linked D-mannuronic acid and β-(1−4)-linked L-guluronic acid units, which exist widely in brown seaweeds such as species of *Ascophyllum*, *Durvillaea*, *Ecklonia*, *Laminaria*, *Lessonia*, *Macrocystis*, and *Turbinaria* [61].

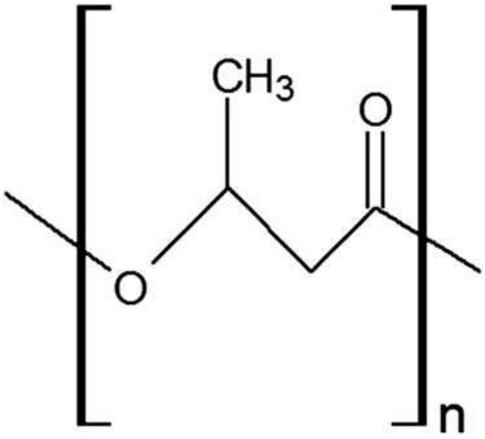


FIGURE 18.8 Chemical structure of PHB.

Alginates are the most commonly used bioink at present, which has good formability and mechanical properties. The main disadvantage of alginate is its chemical structure being unfriendly to cell adhesion, leading to relatively weak biocompatibility [2]. The hydrophilicity, biocompatibility, and liquid-absorbing capacity make alginate an attractive material for wound dressings.

18.5 Final considerations

Among the many producing techniques that have been lately developed, 3D printing enables precise control over the structure, geometry, compositions, spatial distributions, and architectural complexity. The most important 3D-printed polymers are PLA, PCL, PEG, and alginates. The wide use of 3D technology in medical and pharmaceutical applications of these polymers may result in the cost reducing of designing, implementing and using new therapeutic methods and optimizing the existing methods, acceleration of the dynamics of personalized medicine development, improving the "matching" of medical products (tools, implants, orthopedic supplies, drugs, and others) to the specific therapy or disease of the patient. The market for 3D-printed polymeric implantable drug delivery devices is also growing but there are significant obstacles to the rapid development of printed pharmaceuticals, such as the long processing time and the drug's lack of resistance to exposure times at the high temperatures at which the drug is processed.

References

[1] X. Li, R. Cui, L. Sun, K. Aifantis, Y. Fan, Q. Feng, F. Cui, F. Watari, 3D-Printed biopolymers for tissue engineering application, Int. J. Poly. Sci. 2014 (2014).

[2] Z. Gu, J. Fu, H. Lin, Y. He, Development of 3D bioprinting: from printing methods to biomedical applications, Asian J. Pharm. Sci. 15 (2020) 529–557.

[3] L.G. Zhang, J.P. Fisher, K. Leong, 3D Bioprinting and Nanotechnology in Tissue Engineering and Regenerative Medicine, Academic Press, 2015.

[4] E.S. Bishop, S. Mostafa, M. Pakvasa, H.H. Luu, M.J. Lee, J.M. Wolf, G.A. Ameer, T.-C. He, R.R. Reid, 3-D bioprinting technologies in tissue engineering and regenerative medicine: current and future trends, Genes Dis. (2017) 185–195.

[5] C. González-Henríquez, M. Sarabia-Vallejos, J. Rodriguez-Hernandez, Polymers for additive manufacturing and 4D-printing: materials, methodologies, and biomedical applications, Prog. Polym. Sci. 94 (2019) 57–116.

[6] J.Y. Park, J. Jang, H.-W. Kang, 3D Bioprinting and its application to organ-on-a-chip, Microelectron. Eng. 200 (2018) 1–11.

[7] T.J. Gutiérrez, 3D printing of biopolymers: trends and opportunities for medical applications, in: Handbook of Biopolymers Advances and Multifaceted Applications, Jenny Stanford Publishing, 2018.

[8] J. Li, 3D printing of hydrogels: rational design strategies and emerging biomedical applications, Mater. Sci. Eng. R (2020) 1–76.

[9] W. Jamróz, J. Szafraniec, M. Kurek, R. Jachowicz, 3D printing in pharmaceutical and medical applications – recent achievements and challenges, Pharmaceut. Res. 35 (9) (2018) 176.

[10] P. Datta, A. Barui, Y. Wu, V. Ozbolat, K.K. Moncal, I.T. Ozbolat, Essential steps in bioprinting: from pre- to post-bioprinting, Biotechnol. Adv. (2018) 1481–1504.

[11] S.C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, Polymers for 3D printing and customized additive manufacturing, Chem. Rev. (2017) 10212–10290.

[12] S. Vijayavenkataraman, W.-C. Yan, W.F. Lu, C.-H. Wang, J. Ying Hsi Fuh, 3D bioprinting of tissues and organs for regenerative medicine, Adv. Drug Deliv. Rev. 132 (2018) 296–332.

[13] P. Gatenholm, H. Martinez, E. Karabulut, M. Amoroso, L. Kölby, K. Markstedt, E. Gatenholm, I. Henriksson, Development of nanocellulose-BasedBioinks for 3D bioprinting of soft tissue, in: 3D Printing and Biofabrication, Springer International Publishing, 2018, pp. 331–352.

[14] D.W. Hutmacher, M.A. Woodruff, Composite scaffolds for bone engineering, in: Handbook of Engineering Biopolymers, Hanser, 2007.

[15] A. Ghosal, A. Mishra, S. Tiwari, Polymers and nanocomposites for biomedical applications, in: Biopolymers and Nanocomposites for Biomedical and Pharmaceutical Applications, Nova Science Publishers, Inc., 2017.

[16] Z.Z. Denchev, Biodegradation studies of polymer blends and composites comprising biopolymers, in: S. Fakirov, D. Bhattacharyya (Eds.), Handbook of Engineering Biopolymers, Carl Hanser Verlag GmbH & Co. KG, 2007, pp. 799–846.

[17] B. Ostrowska, Trójwymiarowe rusztowania tkankowe z polikaprolaktonu o zmiennej architekturze wewnetrznej do regeneracji tkanki kostnej wytworzone metodą przyrostowego kształtowania, 2015. Warszawa.

[18] J. Liu, L. Sun, W. Xu, Q. Wang, S. Yu, J. Sun, Current advances and future perspectives of 3D printing natural-derived biopolymers, Carbohydr. Polym. (2019) 297–316.

[19] G. Turnbull, J. Clarke, F. Picard, P. Riches, L. Jia, F. Han, B. Li, W. Shu, 3D bioactive composite scaffolds for bone tissue engineering, Bio. Mater. 3 (3) (2018) 278–314.

[20] E.Y. Teo, S.-Y. Ong, M.S.K. Chong, Z. Zhang, J. Lu, S. Moochhala, B. Ho, S.-H. Teoh, Polycaprolactone-based fused deposition modeled mesh for delivery of antibacterial agents to infected wounds, Biomaterials (2011) 279–287.

[21] L. Rojas-Martínez, C. Flores-Hernandez, L. López-Marín, A. Martinez-Hernandez, S. Thorat, C.R. Vasquez, A.D. Rio-Castillo, C. Velasco-Santos, 3D printing of PLA composites scaffolds reinforced with keratin and chitosan: effect of geometry and structure, Eur. Polym. J. 141 (2020).

[22] M. Gutiérrez-Sánchez, V.A. Escobar-Barrios, A. Pozos-Guillén, D. Escobar-García, RGD-functionalization of PLA/starch scaffolds obtained by electrospinning and evaluated in vitro for potential bone regeneration, Mater. Sci. Eng. C 96 (2019) 798–806.

[23] M. Altamimi, S. Neau, Investigation of the in vitro performance difference of drug-Soluplus® and drug-PEG 6000 dispersions when prepared using spray drying or lyophilization, Saudi Pharmaceut. J. 25 (2017) 419–439.

[24] D. Aki, S. Ulag, S. Unal, M. Sengor, N. Ekren, L. Chi-Chang, H. Yılmazer, C. Ustundag, D. Kalaskar, O. Gunduz, 3D printing of PVA/hexagonal boron nitride/bacterial cellulose composite scaffolds for bone tissue engineering, Mater. Des. 196 (2020) 1–9.

[25] M. Mehrpouya, H. Vahabi, M. Barletta, P. Laheurte, V. Langlois, Additive manufacturing of polyhydroxyalkanoates (PHAs) biopolymers: materials, printing techniques, and applications, Mater. Sci. Eng. C 127 (2021) 1–13.

[26] S. Vanaei, M. Parizi, S. Vanaei, F. Salemizadehparizi, H. Vanaei, An overview on materials and techniques in 3D bioprinting toward biomedical application, Eng. Regen. 2 (2021) 1–18.

[27] A. Mora-Boza, M. Puertas-Bartolomé, B. Vázquez-Lasa, J. San Román, A. Pérez-Caballer, M. Olmeda-Lozano, Contribution of bioactive hyaluronic acid and gelatin to regenerative medicine. Methodologies of gels preparation and advanced applications, Eur. Polym. J. 95 (2017) 11–26.

[28] K. Markstedt, A. Mantas, I. Tournier, H. Martinez Avila, D. Hagg, P. Gatenholm, 3D bioprinting human chondrocytes with nanocellulose-alginate bioink for cartilage tissue engineering applications, Biomacromolecules (2015) 1489–1496.

[29] A. Khademhosseini, G. Camci-Unal, 3D Bioprinting in Regenerative Engineering: Principles and Applications, CRC Press, 2018.

[30] D. Nguyen, D.A. Hägg, A. Forsman, J. Ekholm, P. Nimkingratana, C. Brantsing, T. Kalogeropoulos, S. Zaunz, S. Concaro, M. Brittberg, A. Lindahl, P. Gatenholm, A. Enejder, S. Simonsson, Cartilage tissue engineering by the 3D bioprinting of iPS cells in a nanocellulose/alginate bioink, Sci. Rep. 7 (2017).

[31] L.K. Narayanan, P. Huebner, M.B. Fisher, J.T. Spang, B. Starly, R.A. Shirwaiker, 3D-bioprinting of polylactic acid (PLA) nanofiber–alginate hydrogel bioink containing human adipose-derived stem cells, ACS Biomater. Sci. Eng. (2016) 1732–1742.

[32] J. Li, Y. Zhang, J. Enhe, B. Yao, Y. Wang, D. Zhu, Z. Li, W. Song, X. Duan, X. Yuan, X. Fu, S. Huang, Bioactive nanoparticle reinforced alginate/gelatin bioink for the maintenance of stem cell stemness, Mater. Sci. Eng. C 126 (2021).

[33] V. Malkoc, Challenges and the future of 3D bioprinting, J Biomed Imag Bioeng 2 (2018) 64–65.

[34] H. Cui, S. Miao, T. Esworthy, X. Zhou, S.-j. Lee, C. Liu, Z.-x. Yu, J.P. Fisher, M. Mohiuddin, L.G. Zhang, 3D bioprinting for cardiovascular regeneration and pharmacology, Adv. Drug Deliv. Rev. 132 (2018) 252–269.

[35] S.V. Murphy, A. Skardal, A. Atala, Evaluation of hydrogels for bio-printing applications, J. Biomed. Mater. Res. (2013) 272–284.

[36] A.R. Unnithan, A. Sasikala, C.H. Park, C.S. Kim, Biomimetic Nanoengineered Materials for Advanced Drug Delivery, Elsevier, 2019.

[37] S. Lamichhane, S. Bashyal, T. Keum, G. Noh, J. Eun Seo, R. Bastola, J. Choi, D. Hwan Sohn, S. Lee, Complex formulations, simple techniques: can 3D printing technology be the Midas touch in pharmaceutical industry? Asian J. Pharm. Sci. 14 (5) (2019) 465–479.

[38] S.A. Stewart, J. Domínguez-Robles, R.F. Donnelly, E. Larrañeta, Implantable polymeric drug delivery devices: classification, manufacture, materials, and clinical applications, Polymers 10 (2018) 1–24.

[39] Center for Drug Evaluation and Research, Approval Package for Application Number: 207958Orig1s000, 2018. Available from, https://www.accessdata.fda.gov/drugsatfda_docs/nda/2015/207958Orig1s000Approv.pdf.

[40] J. Wang, Y. Zhang, N.H. Aghda, A. Pillai, R. Thakkar, A. Nokhodchi, M. Maniruzzaman, Emerging 3D printing technologies for drug delivery devices: current status and future perspective, Adv. Drug Deliv. Rev. 174 (2021) 294–316.

[41] M.H. Nadhif, H. Assyarify, I. Muhammad, M. Suhaeri, Recent advances in 3D printed wound dressings, AIP Conf. Proc. 2344 (2021).

[42] M. Milojević, G. Harih, V. Boštjan, J. Vajda, L. Gradišnik, T. Zidarič, K. Stana Kleinschek, U. Maver, T. Maver, Hybrid 3D printing of advanced hydrogel-based wound dressings with tailorable properties, Pharmaceutics 13 (2021).

[43] W. Jie, A. Goyanes, S. Gaisford, A. Basit, Stereolithographic (SLA) 3D printing of oral modified-release dosage forms, Int. J. Pharm. 503 (1–2) (2016) 207–212.

[44] W. Jamróz, M. Kurek, E. Łyszczarz, J. Szafraniec, J. Knapik-Kowalczuk, K. Syrek, M. Paluch, R. Jachowicz, 3D printed orodispersible films with aripiprazole, Int. J. Pharm. 533 (2017).

[45] X. Xu, J. Zhao, M. Wang, L. Wang, J. Yang, 3D printed polyvinyl alcohol tablets with multiple release profiles, Sci. Rep. 9 (2019).

[46] J. Skowyra, K. Pietrzak, M. Alhnan, Fabrication of extended-release patient-tailored prednisolone tablets via fused deposition modelling (FDM) 3D printing, Eur. J. Pharmaceut. Sci. 68 (2015) 11–17.

[47] J. Holländer, N. Genina, H. Jukarainen, M. Khajeheian, A. Rosling, E. Mäkilä, N. Sandler, Three-dimensional printed PCL-based implantable prototypes of medical devices for controlled drug delivery, J. Pharmaceut. Sci. 105 (2016) 2665–2676.

[48] N.F. Zaaba, M. Jaafar, A review on degradation mechanisms of polylactic acid: hydrolytic, photodegradative, microbial, and enzymatic degradation, Polym. Eng. Sci. 60 (9) (2020) 2061–2075.

[49] L. Lim, H. Tsuji, Poly(lactic Acid): Synthesis, Structures, Properties, Processing, and Applications, Wiley, 2010.

[50] N. Shimpi, Biodegradable and Biocompatible Polymer Composites: Processing, Properties and Applications, Woodhead Publishing, 2017.

[51] H.-J. Endres, A. Siebert-Raths, Engineering Biopolymers, Hanser, 2011.

[52] A. Lett, S. Sagadevan, S. Paiman, F. Mohammad, R. Schirhagl, E. Léonard, S.F. Alshahateet, W.-C. Oh, Exploring the thumbprints of Ag-hydroxyapatite composite as a surface coating bone material for the implants, J. Mater. Res. Technol. 9 (6) (2020) 12824–12833.

[53] S.-D. Yoon, Y.-S. Kwon, K.-S. Lee, Biodegradation and biocompatibility of poly L-lactic acid implantable mesh, Int. Neurourol. J. 21 (2017) 48–54.

[54] E. Hendrick, M. Frey, Increasing surface hydrophilicity in poly(lactic acid) electrospun fibers by addition of pla-b-peg Co-polymers, J. Eng. Fibers Fabr. 9 (2) (2014) 153–164.

[55] J. Ren, Biodegradable Poly(Lactic Acid): Synthesis, Modification, Processing and Applications, Springer, 2010.

[56] R. Al-Itry, K. Lamnawar, A. Maazouz, Biopolymer blends based on poly (lactic acid): shear and elongation rheology/structure/blowing process relationships, Polymers 7 (5) (2015) 939–962.

[57] Y. Yang, H. Xu, X. Yu, Lightweight Materials from Biofibers and Biopolymers, American Chemical Society, 2014.

[58] H. Vanaei, M. Shirinbayan, S. Vanaei, J. Fitoussi, S. Khelladi, A. Tcharkhtchi, Multi-scale damage analysis and fatigue behavior of PLA manufactured by fused deposition modeling (FDM), Rapid Prototyp. J. 27 (2021) 371–378.

[59] H. Vanaei, K. Raissi, M. Deligant, M. Shirinbayan, J. Fitoussi, S. Khelladi, A. Tcharkhtchi, Toward the understanding of temperature effect on bonding strength, dimensions and geometry of 3D-printed parts, J. Mater. Sci. 55 (2020) 14677–14689.

[60] R. Levato, J. Visser, J. Planell, E. Engel, J. Malda, M. Mateos-Timoneda, Biofabrication 6 (2014).

[61] H. Cui, W. Zhu, M. Nowicki, X. Zhou, A. Khademhosseini, L. Zhang, Hierarchical fabrication of engineered vascularized bone biphasic constructs via dual 3D bioprinting: integrating regional bioactive factors into architectural design, Adv.Healthc. Mater. 5 (2016) 2174–2181.

[62] L. Li, D.V. LaBarbera, 3D high-content Screening of organoids for drug discovery, Comp. Med. Chem. III (2016) 388–415.

[63] J. Idaszek, Ternary Composite Scaffolds with Various Degradation Rates for Bone Tissue Regeneration, PhD thesis, Publishing House of the Warsaw University of Technology, Warszawa, 2016.

[64] M.A. Woodruff, et al., The return of a forgotten polymer – polycaprolactone in the 21st century, Prog. Polym. Sci. (35) (2010) 1217–1256.

[65] M. Labet, W. Thielemans, Synthesis of polycaprolactone: a review, Chem. Soc. Rev. 38 (2009) 3484–3504.

[66] R. Cameron, A. Kamvari-Moghaddam, Synthetic Bioresorbable Polymers, Woodhead Publishing, 2012.

[67] Ż. Górecka, J. Idaszek, D. Kołbuk, E. Choińska, A. Chlanda, W. Święszkowski, The effect of diameter of fibre on formation of hydrogen bonds and mechanical properties of 3D-printed PCL, Mater. Sci. Eng. C 114 (2020).

[68] E. Walejewska, J. Idaszek, M. Heljak, A. Chlanda, E. Choinska, V. Hasirci, W. Swieszkowski, The effect of introduction of filament shift on degradation behaviour of PLGA- and PLCL-based scaffolds fabricated via additive manufacturing, Polym. Degrad. Stabil. 171 (2020).

[69] J.M. Williams, A. Adewunmi, R.M. Schek, C.L. Flanagan, P.H. Krebsbach, S.E. Feinberg, S.J. Hollister, S. Das, Bone tissue engineering using polycaprolactone scaffolds fabricated via selective laser sintering, Biomaterials (2005) 4817–4827.

[70] D. Hutmacher, T. Schantz, I. Zein, K. Ng, S. Teoh, K. Tan, Mechanical properties and cell cultural response of polycaprolactone scaffolds designed and fabricated via fused deposition modeling, J. Biomed. Mater. Res. (2001) 203–216.

[71] K.C. Scheiner, F. Coulter, R.F. Maas-Bakker, G. Ghersi, T.T. Nguyen, R. Steendam, G.P. Duffy, W.E. Hennink, E.D. O'Cearbhaill, R.J. Kok, Vascular endothelial growth factor–releasing microspheres based on poly(ε-caprolactone-PEG-ε-caprolactone)-b-poly(L-lactide) multiblock copolymers incorporated in a three-dimensional printed poly(dimethylsiloxane) cell macroencapsulation device, J. Pharmaceut. Sci. (2020) 863–870.

[72] Q. Yao, B. Wei, Y. Guo, C. Jin, X. Du, C. Yan, Design, construction and mechanical testing of digital 3D anatomical data-based pcl-ha bone tissue engineering scaffold, J. Mater. Sci. Mater. Med. (2015) 5360.

[73] H.-W. Kang, S. Lee, I. Kap Ko, C. Kengla, J. Yoo, A. Atala, A 3D bioprinting system to produce human-scale tissue constructs with structural integrity, Nat. Biotechnol. 34 (2016) 312–319.

[74] X. T, B. KW, A. MZ, D.D. Z. W, Y. JJ, Hybrid printing of mechanically and biologically improved constructs for cartilage tissue engineering applications, Biofabrication 5 (2013).

[75] B.M. Wu, S.W. Borland, R.A. Giordano, L.G. Cima, E.M. Sachs, Solid free-form fabrication of drug delivery devices, J. Contr. Release (1996) 77–87.

[76] L. Viidik, J. Vesala, R. Laitinen, O. Korhonen, J. Ketolainen, J. Aruväli, K. Kirsimäe, K. Kogermann, J. Heinämäki, I. Laidmäe, T. Ervasti, Preparation and characterization of hot-melt extruded polycaprolactone-based filaments intended for 3D-printing of tablets, Eur. J. Pharmaceut. Sci. 158 (2021).

[77] A. Kosik-Kozioł, M. Heljak, W. Święszkowski, Mechanical properties of hybrid triphasic scaffolds for osteochondral tissue engineering, Mater. Lett. 261 (2020).

[78] T. Hoang Thi, E. Pilkington, D. Nguyen, J. Lee, K. Park, N. Truong, The importance of poly(ethylene glycol) alternatives for overcoming PEG immunogenicity in drug delivery and bioconjugation, Polymers 12 (2020) 1–21.

[79] M. Harris, S. Zalipsky, Poly(Ethylene Glycol) Chemistry and Biological Properties, American Chemical Society, 1997.

[80] M. Puri Sikka, V.K. Midha, The role of biopolymers and biodegradable polymeric dressings in managing chronic wounds, in: Advanced Textiles for Wound Care, The Textile Institute, 2019.

[81] A. Aied, W. Song, W. Wang, A. Baki, A. Sigen, 3D bioprinting of stimuli-responsive polymers synthesised from DE-ATRP, Bioprinting (2018) 37–43.

[82] M. Castilho, D. Feyen, M. Flandes-Iparraguirre, G. Hochleitner, J. Groll, P.A.F. Doevendans, T. Vermonden, K. Ito, J.P.G. Sluijter, J. Malda, Melt electrospinning writing of poly-hydroxymethylglycolide-co-ε-caprolactone-based scaffolds for cardiac tissue engineering, Adv. Healthc. Mater. 6 (2017) 1–9.

[83] H. Seyednejad, D. Gawlitta, R. Kuiper, A. de Bruin, C. van Nostrum, T. Vermonden, W. Dhert, W. Hennink, In vivo biocompatibility and biodegradation of 3D-printed porous scaffolds based on a hydroxyl-functionalized poly(ε-caprolactone), Biomaterials 33 (2012) 4309–4318.

[84] T. Pereira, M. Oliveira, I. Maia, J. Silva, M. Costa, R. Thiré, 3D printing of poly(3-hydroxybutyrate) porous structures using selective laser sintering, Macromol. Symp. 319 (2012) 64–73.

PART IV

Polymer market in 3D printing

CHAPTER

19

Global market structure

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19.1 Introduction

Polymers are some of the most used materials in 3D printing, and due to a variety of printing techniques, myriad types of polymers are available on the market [1—3]. 3D printers are used not only for industrial and prototype but also in education, public libraries, university classrooms and laboratories, and ultimately in homes. New polymer-based materials are constantly introduced, and the existing ones are improved and combined to fulfill specific requirements of the future manufactured product. This practice has a significant impact on the further development of the 3D printing market structure and bringing this uprising technology one step closer to conventional industrial manufacturing.

The accessibility of 3D printers for industrial as well as for domestic purposes has marked significant growth between 2010 and 2019. Global sales of industrial-scale and consumer-based printers, devices, materials, and services have grown by an annual average of more than 33% over the period of 2010—2013 to a total of $1.4 billion in 2014 [3] and 32.3% over the period of 2013—2019 with a total of $8.2 billion in 2018 [4—6]. This trend shows that demands in the field of additive manufacturing (AM) are continually growing.

According to Tofail and colleagues [3] commercial success of AM can be observed through the concept of four Ms: market, materials, making, and metrology. This means that manufactured object needs to serve its intended use in the *market* by using one of the AM routes (*making*) and assuring that properties of used *materials* meet desired and predefined standards, confirmed through appropriate measurement (*metrology*) while maintaining competitive production cost. Authors emphasize that the current market opportunities and the ability to produce objects using a variety of different 3D printing techniques must be well matched with solving materials-related challenges and adaptation of suitable metrology.

Challenges of 3D printing reflect in the development of a safe, robust, user-friendly, sustainable, integrated system to provide required printing parameters such as printing speed, resolution, inner structure, and accurate dimension control. Challenges concerning printed products are surface finish, part size, mechanical, physical and chemical characteristics, and overall product quality between different machines and batches of productions.

19.2 3D printing global value chains

A majority of world manufacturing is the result of an international division of labor coordinated by multinational enterprises (MNEs). MNEs have a capability in the organization and effective coordination of global value chains (GVCs) [7]. Term "global value chain" was introduced by Porter [8] who differentiate between dispersed and concentrated GVC configurations. Concentrated GVC configurations are maybe best illustrated by the emergence of China as the so-called factory of the world [9]. The bulk of electronic equipment, clothing, toys, and domestic appliances is produced in China [10]. This way of concentrated production of goods is moved far away from end-users. With the emergence of the information age, this view is changing [11], which may influence the configuration of GVCs in terms of their geographic span and density. Some authors claim that 3D printing is introducing the next industrial revolution [12], as well as that this technology will lead to a sustainable development for low-income countries and that personal fabrication and peer production will replace most industrial processes [13—15].

Polymers for 3D Printing
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Laplume et al. [16] theorize that the type of materials, the need for customization, speedy delivery, and low cost for printing complex objects might be disruptive drivers of this technology. They emphasized that roughly 70,000 low-cost 3D printers were sold before 2013, and around 145,000 units in 2013. Also, between 2009 and 2013, the RepRap open-source project for the production of DIY 3D printers lowered their market price to less than $1000. Till 2019 this technology improved rapidly, which, as a result, lowered the price of the basic entry-level machine to just a few hundred dollars. The most used material in these open-source printers are plastics and digital print files distributed throughout online repositories (Fig. 19.1) which are mostly intended to be printed in plastic [16].

According to Laplume and colleagues [16], manufacturing of intricate metal products with complex geometries are starting to be affected by AM. Also, metal printing appears in Google Scholar as a rising research topic with inventions and scientific papers increasing at a rate of 55% per year. Research studies about 3D printed ceramics and clay also show a growing pace of about 45% per year. In their research, Laplume and colleagues [16] pointed out that the four parameters seem to explain the extent of the diffusion of 3D printing technology in given manufacturing industry:

- the nature of the industrial process, including the type of input materials,
- the need for speedy delivery,
- the need for product customization and quick responsiveness to changing consumer preferences, and
- the need for low-cost, low-volume products (such as prototypes).

Laplume and colleagues [16] are trying to give answers to questions if and how 3D printing technology affects the rationale of separating production from consumption and locating different manufacturing stages at separate sites? Concerning this geographical configuration of GVCs, authors specify three determinants:

- factor cost differentials,
- scale economies, and
- factors that are impeding global specialization, including transportation costs, import barriers, and technological inseparability.

Factor cost differentials refer to labor and capital inputs of manufacturing. These differentials have driven industrial manufacturing to Asia as leading manufacturing continent. Labor cost in Asia and other developing countries is low, so significant percentage of conventional production is situated there. 3D printing has the potential to reduce the need for massive workforce, thus reducing the effects of labor cost and moving production locally to households, local print shops, and online print shops. On the other side, capital-cost differentials are lower than labor cost differentials across countries [17], which means that 3D printing equipment has relatively constant price worldwide. 3D printing, therefore, can be described as capital-intensive production but highly automated and with low labor input [16].

In the scale of economies, production of expensive tools and machines is profitable only if the high volume of the same product will be produced with them. Larger market share means improved productivity and the lower average cost of the product or service. Often job change and customization is not the desired practice in the scale

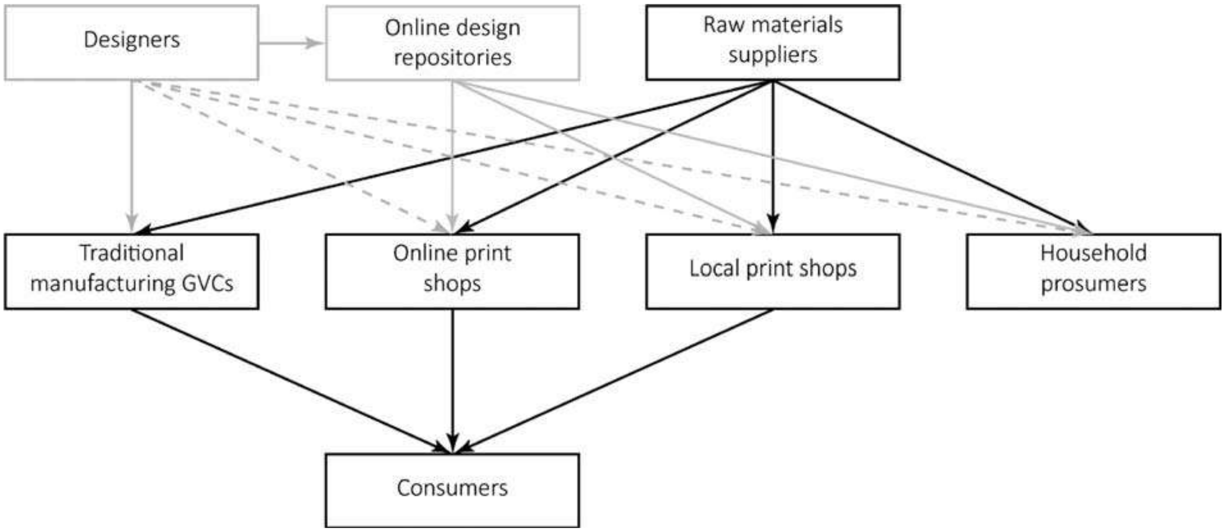


FIGURE 19.1 The 3D printing global value chain. *Adapted with permission from [16].*

of economies. However, 3D printers, as highly generalized machines, are well suited to the task of customization producing a wide range of products without the need for retooling or reconfiguration. They can produce a great variety of products without additional manufacturing costs [18]. Product cost under 3D printing is constant and independent of the scale of production, but it can be said only in industries where great variety and customization of products are needed, product life cycles are short, and delivery times are critical [19]. One of the advantages of 3D printing is the possibility to manufacture the entire product without the need for assembly and reducing the use of intermediate goods. 3D printing allows raw materials to be used and shaped into finished products. This leads to a shortening of value chains by excluding intermediate goods. In recent years, opening more local production sites is common practice due to the adoption of 3D printing which leads to the necessity of more dense and widespread raw material supply system. In other words, one can predict the delivery of small batches to more additive manufacturers. By shortening the value chain by reducing intermediate goods, transportation costs lower. It can be said that adoption of 3D printing technology in an industry leads to development toward shorter and more dispersed GVCs thus creating an environment where manufacturing will become more local and closer to the end-user.

Due to increased need for 3D printing services and products, there is a potential threat of increased proliferation of waste which means that recycling technologies need to keep up the pace with diffusion of 3D printers. This problem already exists with conventional manufacturing and can only be aggravated with the emergence of 3D printing if left neglected.

19.3 Presence of 3D printing techniques on the global market

To analyze polymer global market structure, it is necessary to have a brief insight into the current state of 3D printing overall. In Sculpteo's *The State of 3D Printing*, 2019 edition report [20,21], 1300 people from Europe (58.7%), Asia (20.2%), North America (16%), South America (1.6%), Oceania (1.1%), and Africa (0.8%) participated in a survey about 3D printing. The majority of participants were between 25 and 34 years old (39.1%), from 35 to 44 years old (20.7%), 45 to 54 (16.1%), and above 55 (10.3%). The primary context for using 3D printing is work (60.6%), hobby (21.8%), and studies (17.6%). In the 2020 report [22], 1600 people from Europe (48.1%), North America (28.2%), Asia (13.1%), Africa (5.9%), South America (4%), and Oceania (1%) were involved in 3D printing survey. The majority of participants were between 25 and 34 years old (40%), from 35 to 44 years old (22%), 45 to 54 (15%), and above 55 (11%). The primary context for using 3D printing is work (59%), hobby (24%), and studies (17%). From these demographic data, one can see that there is an increased interest in participating the survey among North and South American and African participants, but slight decline in participation among European and Asian population. This can indicate that, according to data from this report, American and African market segments are growing.

Prototyping and proof of concept dominated 3D printing applications in 2020, but there is a noticeable increase in 3D printing for production from 22% in 2017 up to 49% in 2020. In addition, the utilization of 3D printing for R&D and education has increased to 42%, which corresponds to increased demand for new materials and technologies in the market [22].

One of the most used 3D printing technology, mainly in-house, is Fused deposition modeling (FDM), followed by SLS (mainly via external service) and SLA. 51% of the respondents emphasize that quality control is the top challenge for using 3D printers [22]. 68% of the participants said that they would find more uses or new applications for 3D printing and 55% report that they will start to use new materials. Hence, there is a growing need for inventing new and improving existing material formulations. 44% of participants report that they will start to use new materials in 3D printing over the next year [22]. Respondents are also asked to point out what are the most limiting factors in the adoption of 3D printing. 59% of them emphasized that the cost of entry and 51% of them believe that the knowledge gap is a significant blocker to adopting 3D printing. Operating cost is the third limiting factor of 3D printing with around 36% votes. There are also some interesting questions such as necessities for the growth of the 3D printing industry and important factors affecting the application of 3D printing in the future. Technologies reliability and new materials are necessary for the growth of 3D printing. Most critical factors that affect respondents' 3D printing activities in their businesses are machine capabilities and material supply and costs [22].

Concerning investments in 3D printing, 29% of the respondents stated that they had invested over $100,000 in their 3D printing activity in 2019 and on the second place (28%) were investments from $1000 to $10,000. This means that small investors have a great and almost equal market presence as ones ready to make more significant investments. According to Tofail and colleagues [3], 3D printing is more suitable to high-value low-volume products due to irrelevant impact of unit labor cost or traditional economies of scale. In 2018, 3D printing share in total EU export and private R&D expenditure was both 80%, and it contributes to 1.6 million jobs and 11% of the total EU production. In the United States, 3D printing is used in the majority of manufacturing sectors.

On the global scale, it is estimated that $642.6 million in revenue was recorded for 3D printed goods, with the United States contributing with an estimated $246.1 million or 38% of global production in 2011 [23]. There was approximately 62.8% of all commercial/industrial units sold in 2011 produced by three primary producers of AM systems: Stratasys, Z. Corporation, and 3D Systems. US-based companies were responsible for the manufacturing of around 64.4% of AM systems.

Asia has around 70% manufacturing share of global trade with China as the front-runner in the adoption of AM in Asia. In 2013 it was estimated that China's 3D printing market share was around 9% of the global market with $238.85 million in revenue. With 200,000 3D printers installed in 2013, China contributes around 10% in comparison to 40% US contribution to sales of 3D printers globally [24].

In the IDTechEx research paper [25], BCG matrix (growth–share matrix) for 3D printing is presented. Different markets are classified into four quadrants to define in which of the 3D printing sectors should be invested. Gordon points out that hobbyists and orthopedics are identified as a star with high market growth and high market share. Most profitable are noncritical aerospace, prototyping, and medical market segments, and they are marked as cash cows and should be "milked" to provide as much cash as possible. Problem child (or often called question mark) is the segment with low market share and high market growth which consume a large amount of cash and with potential to gain market share and become a star, and later cash cow. Market segments such as education, military, architecture, jewelry, construction, and automotive are identified as a problem child. Industries such as art, fashion, food, film industry, off-planet manufacturing, and electronics hold low market share and low market growth, and they are identified as dogs. They are usually not worth investing in because they generate low or negative cash returns [26].

According to BCC research staff [4–6] and their report about global market for 3D printing and global market trends in the United States, Canada, Mexico, Japan, China, India, France, Germany, the United Kingdom, Italy, Spain, and Middle East and Africa it was estimated that 3D printing production totaled nearly $2.8 billion in 2013, nearly $3.8 billion in 2014, $3.7 billion in 2016, and $8.4 billion in 2018. In 2015 they predicted compound annual growth rate (CAGR) of 32.2% for the period of 2013–2019, CAGR of 23.2% for the period of 2016–2021, and CAGR of 22.4% for the period of 2018–2023.

The Wohlers Report from 2017 [27] indicates that the 3D printing is a $6.063 billion industry and that AM industry grew by 17.4% in worldwide revenues in 2016, down from 25.9% the year before.

From the report of Prescient & Strategic Intelligence from June 2018 it can be seen that estimated 3D printing market is valued at $8.583 billion in 2017 with the CAGR of 24.6% from 2013 till 2017. However, Wohlers Report from 2018 [28] estimates that 3D printing market value exceeds $7.3 billion and a solid 21% growth of all AM products and services worldwide.

In Markets and Markets report [29], the overall 3D printing market was forecasted to be around $9.9 billion in 2018 with expectations to grow to $34.8 billion by 2024 with CAGR of 23.25%.

3D printing market is categorized into printer, material, software, and service where, according to Prescient & Strategic Intelligence [30], printer held the largest revenue share of over 45% in the printing market in 2017. Polymers, metals, and ceramics are some of the most used materials used in 3D printing, and metal-based 3D printing was the most significant revenue contributor with 49% of the 3D printing materials in 2017. Among seven 3D printing categories introduced by The American Society for Testing and Materials [31] 52900:2015 standard, powder bed fusion process held largest revenue with over 20% market share in 2017 [30].

Geographically, the largest market for 3D printing is North America, with over 35% of revenue in 2017. Implementation of AM technologies in aerospace and defense and health-care industries represents the major factors supporting the growth of the 3D printing market in North America.

In 2017 the market for low-cost desktop 3D printers grew by 49.4% worldwide, compared to 14.9% for 3D printing systems at all price levels [27]. The main use of 3D printing technologies is prototyping, and the most used materials for this job are polymers, but in recent years, manufacturers began improving and expanding the use of metal printing mainly driven by automotive and aerospace industry and their intention of producing end-use parts and components. According to Wohlers Report [27], approximately half of all AM service providers surveyed are running metal 3D printing systems. Besides aerospace and automotive niche, the emergence of the medical and dental segment is noticeable with the contribution of $667 million of $6.063 billion total which is roughly 11% of the overall market revenue in 2017.

In 2017 report from Market and Market [29] it was highlighted that 3D printing service segment would have the largest share of the 3D printing market based on offering due to expected increase in the demand for customized products.

The Wohlers Report from 2018 reveals a significant increase in metal 3D printing. Total market revenue is estimated to be over $7.336 billion, with 21% growth from the last year [28]. Compared to 983 AM systems sold from 2016 to 2017, 1768 metal AM systems were sold in 2017 which is nearly 80% higher. More companies are involved in manufacturing of industrial AM systems (from 97 companies in 2016 to 135 companies in 2017). In 2015 more than 278,000 desktop printers (under $5000) were sold worldwide and in 2018 report this number almost doubled to 528,952 desktop 3D printers. It was estimated in this report that revenue from the desktop segment was over $500 million in 2017.

One of the significant observations in Wohlers Report from 2019 was the growth of around 41.9% of revenue from metal printing which is an indicator of the increasing use of AM for a production application. Also, there is growth in a number of companies which are involved in the manufacturing of industrial AM systems priced at $5000 (from 135 companies in 2017 to 177 in 2018). In 2018 industrial system manufacturers grew noticeably but desktop 3D systems manufacturers (under $5000) noted a significant decline in annual growth.

19.4 Presence of 3D printing materials on the global market

The capabilities of 3D printing technology are presented through the use of different materials available on the market compatible with a variety of printing processes. The range of materials has continuously diversified and continued to expand with end-users demands of higher quality products, greater choice, and flexibility. There is a constant need for materials which can represent the end product's appearance and behavior on the best possible way [32]. Based on Industry 4.0 today's (2019) article and report from Allied Market Research (2016), 3D printing materials market was valued in 2015 at $578 million and their expectation is that this market will reach $1.87 billion by 2022 with CAGR of 18.3% in this period (2014–2022). In recent years, more composite materials are being developed, and existing ones are improved, but among them, polymers are the most commonly used 3D printing material, and it is expected that demand for these materials will grow in the forecast period. Reason for this assumption comes from intensified use of plastics in the manufacturing industry and consumer goods sector. According to this report, polymers are the largest material segment in the global 3D printing materials market. Recently, metal 3D printing materials segment is expected to have the highest CAGR of 24.4% during the forecast period (2015–2022) due to growing penetration of these materials in aerospace, defense, and health-care industries. Altogether, polymers and metals segment are accounted for more than 90% market share in 2015. Geographically, North America accounted in 2015 for almost half of the global demand for 3D printing material, and the Asia-Pacific region tends to experience the fastest growth rate with CAGR of 19.1% during the forecast period. However, one of the concerning factors in the growth of the materials market segment is toxicity to human beings and flora and fauna as well as the high cost of materials. These are the major issues set before further development of 3D printing materials market.

According to research analysis done by IDTechEx, the printer market may eventually saturate, so profit is predicted to be made from materials supply (Fig. 19.2) [25]. In this report, it is also emphasized that the 3D printing industry is moving to production of final parts and that thermoplastic powders and metal powders will gain market share.

In the PR Newswire report (2018) detailed forecast, based on interviews from 90 leading companies in the 3D printing industry, key materials are expected to have a total market value of over $24 billion by 2027 from which $6.6 billion is contributed to the market of thermoplastic filaments.

According to report from Markets and Markets [33], the 3D printing material market size is estimated to grow from $1.5 billion in 2019 to $4.5 billion by 2024 and to $8.7 billion by 2027 with CAGR of 25% during the forecast period. It is predicted that metal 3D printing materials are expected to be the most significant type of 3D printing materials market until 2024. The market for plastic 3D printing materials has a second-largest market position. Concerning the form of 3D printing material, filament form market is estimated to have the highest CAGR during this period. According to Wohlers Report [34], revenue from metals grew an estimated 41.9%. Also, sales of polymer materials for powder bed fusion were at its highest point in 2018.

One of the predictions of IDTechEx (2019) based on the research done with the collaboration of 25 companies eminent in the AM segment is that the global market for 3D printing materials will be worth $23 billion by the year 2029.

According to Sculpteo's report [22], polymers were the most used materials in 2019 especially for printing in-house and tied for the second most used were resins and metals with resins mostly used in house and metals mainly by using external services.

If the group of 3D printing users called Power users, who are using this technology in their work for over 2 years and have invested at least $10,000 in 3D printing in 2019, are observed, we can see that the plastics are most used

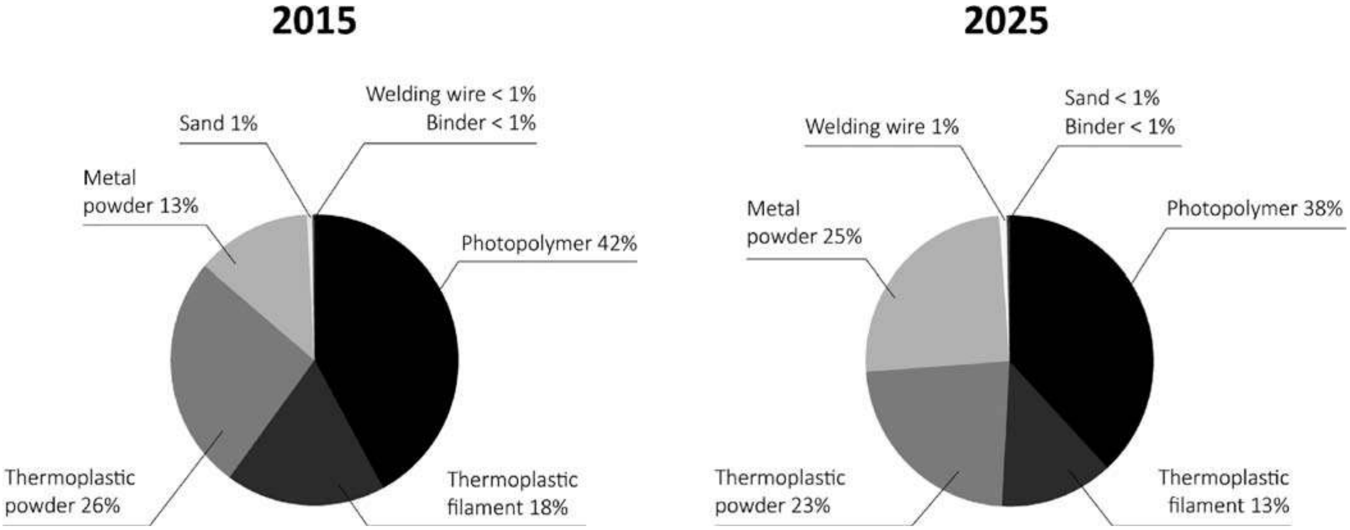


FIGURE 19.2 3D printing materials market share. *Adapted with permission from [25].*

material in 2020 (92% of responses) followed by ceramics (73%) and metals (66%). Sculpteo also reported the state of 3D printing in the last 5 years (from 2015 to 2020). Plastics and metals have similar growth trend with a slower growth rate in the last 2 years. However, resins marked greater growth in 2020. Also, it can be seen that all materials achieved greater consumption in 2019 and 2020 [22].

The basic AM materials such as thermoplastics, photosensitive resins, ceramics, and glass can be combined and reinforced with carbon nanotubes and fibers, biologicals, pharmaceuticals, and others. The main determinants of success in this task are process optimization and selection of process parameters [1]. According to SmartTech [35], the AM market has regained the element of balanced growth. Companies such as 3D Systems and Stratasys see more consistently positive growth results. The success of these two companies helped to contribute to the polymer AM segment growing to an estimated nearly $5.5 billion.

19.5 Current state of polymer 3D printing material manufacturers and services

Polymer materials can be divided into two groups: natural polymers (cellulose, natural rubber, sutures, collagen, deoxyribonucleic acid, and others) which are known for their friendly behavior to the biological environment in which these are used; and synthetic polymers (such as polyethylene (PE), polypropylene (PP), high-density polyethylene (HDPE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyethylene glycol (PEG), polycaprolactone (PCL), polytetrafluoroethylene (PTFE), polyglycolide (PGA), poly(lactide-co-glycolide) (PLGA), ultrahigh-molecular-weight polyethylene (UHMWPE), polylactic acid (PLA), polyetheretherketone (PEEK), polymethyl methacrylate (PMMA), nylon, and others). Some of these synthetic polymers are also biodegradable and environmentally friendly.

As different research papers and reports state it, 3D printing targets mostly the production of polymeric parts and models [1–3]. The majority of 3D printers used for medical purposes in 2014 were systems based on material jetting and vat photopolymerization techniques with polymers as the most commonly used material in the 3D printing market as a whole. As it was said, polymeric materials can be preformed as powder, filament, and sheet, but can also be in the form of photosensitive resins.

There are, for example, a limited number of polymers applicable for SLS, and most of them are based on two basic ones: PA12 and PA11 [36]. In the work of Schmid and Wegener [36] it is presented that polymers for SLS market have a share of around 1900 t/year which is far less than a niche market compared to a total consumption of about 290 Mt/year. This means that for 1 kg of SLS powder, 200 t of other polymeric material is sold at the same time. According to Schmid and Wegener [36], there is room in the SLS market for further development and emergence of new materials. There is a lack of standard polymers and almost no materials from these so-called commodity plastics: PE, PP, PVC, and others are available so far for SLS processing.

According to Grand View Research (2020), the global printing plastics market size was estimated at $579.7 million in 2020 and is expected to expand at a compound annual growth rate of 3.4% from 2021 to 2028. Rising demand from automotive and aerospace as well as health care and hobbyist segments is expected to encourage market growth. In 2017 3D printing plastics in the form of filaments in diameter of 1.75 mm and 3 mm dominated the market in terms of revenue. 3D printing inks, especially the smart inks, are one of the growing market segments and the target of ongoing research and development activities and investments. These inks can change their shape as well as color, enhancing their functionality. According to Grand View's Research [37] report, there is a high demand for 3D printing plastics in the aerospace industry, especially in commercial aircraft production. One of the largest application segments in 2017 was medical, and it is predicted that it will continue to grow due to the growing incidence of vascular and osteoarthritis diseases. It is stated in this report that photopolymers were the most used type in the 3D printing plastics market (around 70%) in 2017 and that it will probably hold its position in the market through 2025. Photopolymers are utilized in inkjet, PolyJet, and vat photopolymerization techniques with polyamide (PA) in the first place (around 8% of market share), followed by PLA, ABS, and ASA (around 6%). Other plastic materials have around 10% of market share. It is estimated that PA is likely to record the highest CAGR of 28.5% during the period from 2017 to 2025. Two different grades of nylon are being used, nylon 6 and nylon 6,6, both with similar ratios of hydrogen, oxygen, nitrogen, and carbon. The largest 3D printing plastic market is North America, with a revenue share of over 40%, followed by Europe and the Asia-Pacific [37].

Various sources such as industry journal *Additive Manufacturing*, 3D Printing Association, databases such as Factiva, and interviews from experts in related industries and suppliers have been used to collect information in the research of Markets and Markets [29]. 3D printing plastic market is estimated to $494.1 million in 2017 and is projected to reach $1.96 billion by 2023, at a CAGR of 26.1% during the forecast period. In 2018 the 3D printing plastic market was estimated to be $615.8 million and is projected to reach $1.96 billion by 2023, at a CAGR of 26.1% between 2018 and 2023. Increasing demand for 3D printing in end-use industries and bio-based plastics affect the 3D printing plastics market positively.

It is estimated in the report from Markets and Markets [38] that 3D printing plastics market is estimated to be $615.8 million in 2018 and that it will reach $1.96 billion by 2023 with a CAGR of 26.1% between 2018 and 2023. Photopolymer segment of the overall plastic market is estimated to have the largest share of the 3D printing materials market in 2018, and it is predicted that it will stay dominant in the market till 2023. The highest CAGR during the period from 2018 to 2023 will belong to PA material.

In the survey conducted by Report Consultant [39], the United States and Europe are the main consumption regions in the 3D printing market. In 2016, these two regions occupied 54.57% of the global total consumption volume. According to this report, 3D printing polymer market is valued at $300 million in 2018 and will reach $370 million by the end of 2025 with a CAGR of 2.5% during the evaluation period.

The report from SmartTech Analysis [40] emphasizes that 3D printing polymer market will reach $3.2 billion by 2022, with 750 million cubic inches of plastic parts being printed. Of the total 3D printing polymer market photopolymers will contribute $1.7 billion and thermoplastic materials with around $1.4 billion in revenues in 2022. Fig. 19.3 represents polymer materials market size and sales growth in the period from 2014 till 2026.

With propagation of 3D printing there are currently many material manufacturers present on the market. In Table 19.1, major 3D printing materials manufacturers in 2019 are presented.

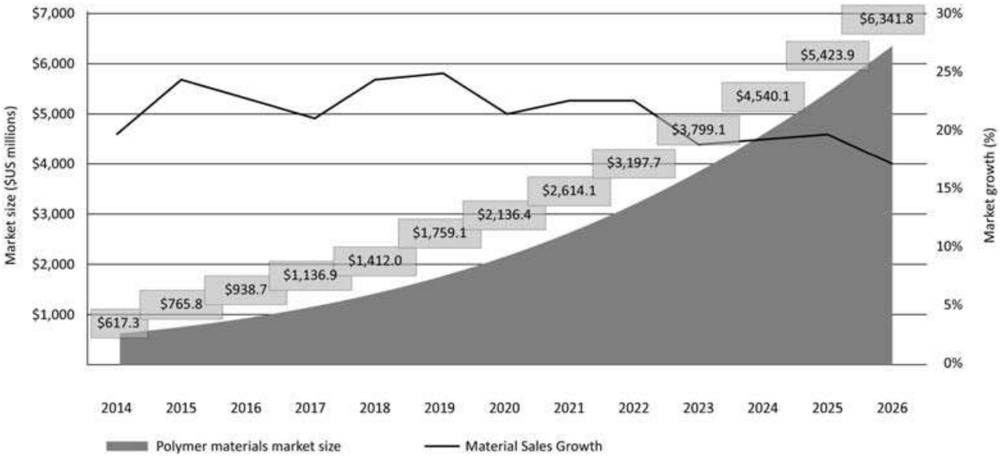


FIGURE 19.3 Polymer materials market size and sales growth from 2014 to 2026. *Adapted with permission from [41].*

TABLE 19.1 Major 3D printing materials manufacturers in 2019 [25,29,30,33,38,39].

Photopolymer manufacturers	Thermoplastic filaments manufacturers	Thermoplastic powders manufacturers
Asiga, B9Creator, Bucktown Polymers, Carima, DWS systems, Envisiontec GmbH, Kevvox, Maker Juice Labs, Rahn AG, Sartomer, Stratasys Ltd., 3D Systems Corporation, ExOne, MicroFab, Solidscape, CMET Inc., Somos, Lithoz, Prodways, Wuhan Binhu Mechanical & Electrical Co. Ltd.	3D Systems Corporation, Airwolf 3D, ColorFabb, Esun, Faberdashery, Markforge3D, MakerBot Industries, Inventrables, MadeSolid, Stratasys Ltd., KDI Polymer specialists Ltd., Taulman 3D, Verbatim, UP-3D, LuxExcel, RepRap, Solidscape, Argyle, Materials Inc., Polymakers	Alm, Arzauno Sintering Materials, CRP Group, EOS GmbH, Electro Optical, Exceltec, Graphite, Taulman 3D, 3D systems Corporation, Paramount product Development Specialists, Farsoon Technologies, LuxExcel, Wuhan Binhu Mechanical & Electrical Co. Ltd., ConceptLaser, Asiga, Keyence Corporation

There are many well-established and emerging companies that provide 3D printing services. They can print objects on-demand using different 3D printing machines and a variety of materials to accommodate the requirements of end-users and their uploaded 3D models. These services can be the right solution for companies that want to try implementing AM in their workflow or if their needs are modest to be profitable acquiring their 3D printer. Some of the 3D printing services are presented in Table 19.2.

TABLE 19.2 The 3D printing services and hubs [20,21,42–49].

3D Print services and hubs	Capabilities
Shapeways https://business.shapeways.com/partnership	Selective Laser Sintering (SLS), Multi Jet Fusion (MJF), PolyJet, Digital Light Synthesis (DLS), Binder Jetting
Sculpteo https://www.sculpteo.com/en/3d-printing/	Selective Laser Sintering (SLS), Multi Jet Fusion (MJF), PolyJet, CLIP (DLS), Colorjet, Selective Laser Melting (metal), Direct Metal Laser Sintering (Metal), Binder Jetting (metal), Casting (metal)
3D Hubs https://www.3dhubs.com/3d-printing/	Fused Deposition Modeling (FDM), Stereolithography (SLA), Selective Laser Sintering (SLS), Multi Jet Fusion (MJF), Direct Metal Laser Sintering (DMLS), PolyJet
i.Materialise https://i.materialise.com/en/3d-printing-technologies	Fused Deposition Modeling (FDM), Stereolithography (SLA), Selective Laser Sintering (SLS), Multi Jet Fusion (MJF), Direct Metal Laser Sintering (DMLS), PolyJet, Lost Wax Printing & Casting, Indirect Metal Printing (Binder jetting)
Protolabs https://www.protolabs.com/services/	Direct Metal Laser Sintering (DMLS), Stereolithography (SLA), Carbon DLS, Multi Jet Fusion (MJF), Selective Laser Sintering (SLS), PolyJet
3D Printing.com https://3dprinting.com/3d-printing-service/	Stereolithography (SLA), Direct Light Processing (DLP), Selective Laser Sintering (SLS), Drop on Demand (DOD), Selective Laser Melting (SLM), Direct Metal Laser Sintering (DMLS), Digital Light Synthesis (DLS), Fused Deposition Modeling (FDM)
Makexyz (3D printing hub) https://www.makexyz.com/	Finds a location with 3D printer near the customer and ships end part
Xometry https://www.xometry.com/	Carbon DLS, Direct Metal Laser Sintering (DMLS), Fused Deposition Modeling (FDM), Multi Jet Fusion (MJF), PolyJet, Selective Laser Sintering (SLS), Stereolithography (SLA)
JawsTec https://www.jawstec.com/3d-printing-capabilities/	Multi Jet Fusion (MJF), Selective Laser Sintering (SLS), Stereolithography (SLA)

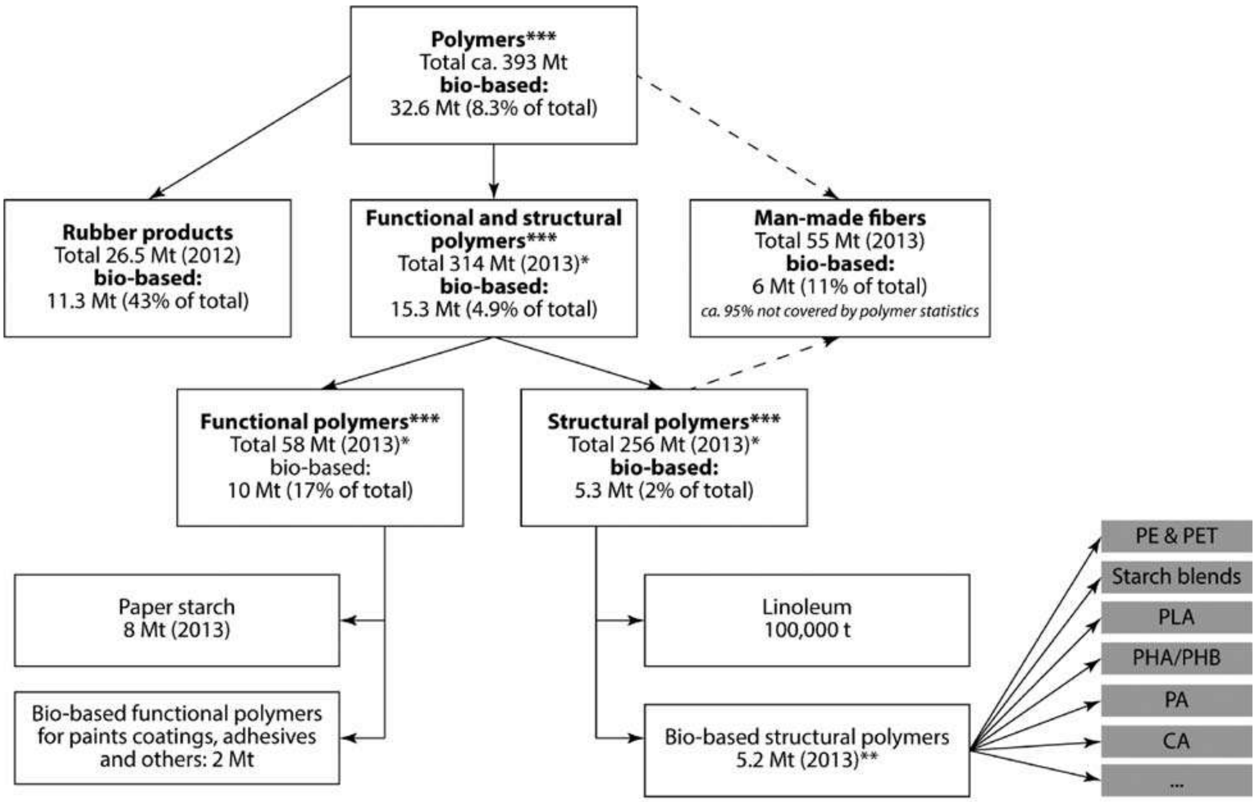
19.6 Current market presence of bio-based polymers

One of the advantages of bio-based polymers is that they replace fossil carbon in the production process with renewable carbon from biomass. The second advantage is in biodegradability of about a quarter of bio-based polymers, but this depends on the environmental conditions. This means that unused plastics that cannot be collected can biodegrade once entered in the environment without leaving behind microplastics [50]. According to the research on bio-based building blocks and polymers in the world [51], the market was dominated by bio-based and nonbiodegradable polymers with a bio-based PET and PE as leaders.

The bio-based polymers production capacities by the selection of European Bioplastics were estimated to 1.6 million tonnes in 2013, 7.2 million tons in 2017 [51], and 7.5 million tons in 2018 [50]. However, in the most recent report from Skoczinski and associates [52] in 2019 bio-based polymers production capacities were estimated to 3.8 million tons, and 4.2 million tons in 2020.

The capacities and production of bio-based polymers will continue to grow with an estimated CAGR of about 8% until 2025, which is about the same as petrochemical polymers and plastics. The increased capacity and production from 2019 to 2020 is, according to report, due to expansion in polylactic acid (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) production in Asia and worldwide epoxy resin production. Estimation is that capacities for PAs and polypropylene (PP) will continue to grow significantly (about 36%) until 2025. Capacity for production of casein polymers in Europe will increase by 32%, PE by 8%, and PLA and PBAT by 7% until 2025.

With largest bio-based production capacities installed worldwide (47% of the market), Asia is the leading region in 2020. Europe follows with 26%, North America with 17%, and South America with 9%. Asia also displays the highest growth of bio-based polymer capacities compared to other regions of the world with expected CAGR of 16% between 2020 and 2025. This increase is mainly due to higher production capacities for PA, PBAT, PHA, and PLA. The total share of worldwide bio-based polymers compared to fossil-based is presented in Fig. 19.4.



(*): Data from PlasticsEurope 2014. Original data show 299 Mt for 2013 in total. When the same shares as 2011 (PlasticsEurope, 2012) this would mean: 251 Mt structural polymers and 48 Mt functional polymers plus bio-based polymers (nova, 2015);
(**): nova-Institute 2015;
(***): Polymers covering thermoplastic and thermosets; Different additional sources, like international Rubber Study Group (www.macpls.it, 13-07-10), The Fiber Year 2014 (14-05)

FIGURE 19.4 Polymers worldwide with bio-based shares in 2013. *Adapted with permission from [51].*

In contrast to bio-energy and bio-fuels, there is lack of European policy framework (quotas, tax incentives, green electricity regulations, market introduction programs, and others) which puts European union in a relatively weak position in the production of bio-based polymers [50]. According to Skoczinski and associate (2021), the largest share (24%) of actually produced bio-based polymers belongs to fibers including woven, nonwoven (mainly cellulose acetate (CA) and polytrimethylene terephthalate (PTT)) in 2020, followed by the packaging, flexible, and rigid, also with 24% share in total, the automotive and transport sector with 16% (mainly epoxy resins, PUR, and aliphatic polycarbonates (APCs)), building and construction sector with 14% (mainly epoxy resins and PA), consumer goods with 9% (mainly starch-containing polymer compounds, PP, and casein polymers). The agriculture and horticulture, electrics and electronics, as well as functional and others have a market share of under 5%.

19.7 Innovative approaches and novelties in material production

One of the main concerns about production and application of polymers and plastics used in 3D printing and in general are health issues and negative impact on the environment. New materials are being developed, and there are many initiatives on the topic of lowering risks of damaging our environment and health in the utilization of 3D printing, application, and afterlife of 3D printed products. Kucherov, Gordeev, Kashin, and Ananikov [53] investigated the use of poly(ethylene-2,5-furandicarboxylate) (PEF), which is an entirely biomass-derived green polymer in 3D printing. Researchers evaluated a process for synthesizing a polymeric material from biomass and found out that objects printed with PEF can be wholly recycled (melted, converted to the filament, and used in 3D printing again) without notable degradation of the polyester. There was no visible drop in printing quality, no change in composition/oxidation, and it was able to get high-resolution prints, and most of all, it was fully compatible with carbon-neutral concepts. Some of the biodegradable materials for 3D printing are PLA, PHA, polyvinyl alcohol (PVA), PET, and HIPS [54].

There are many research topics related to the development of 3D printing composite materials with enhanced physical, chemical, and mechanical properties by adding filler materials such as aluminum oxide, aluminum, copper, ceramics, and natural fibers, in a polymeric matrix. Many different biocomposite filaments are available on the market. They are usually a mixture of some bio-based and/or biodegradable polymer matrices such as PLA and bio-based fillers (sawdust, cellulose fibers, or other natural fibers). Many "inside-laboratory" composite materials are being developed and investigated in order to solve some of the sustainability problems. One of the examples is from the work of Kuo and colleagues [55] who prepared biomass mixture of thermoplastic starches (TPSs) and ABS with TiO_2 particles for use in FDM 3D printing technique. In the work of Ceccolini [56], the new biodegradable and nontoxic material AgriDust was created. It is composed of food waste (64.5%) and a binder made from potato starch and can be extruded using standard extruder with a syringe and no heat. Students from Purdue University in Indiana, US [57], developed soy-based filament named FilaSoy composed of PLA and 20%–25% of soy additive which improves PLA performances by providing antimicrobial properties and reducing brittleness. Zhang and colleagues [58] have mixed graphite flakes and PLA filament to create high conductive PLA material. Today, there are many commercially available conductive materials, materials with improved mechanical, thermal, physical, and chemical properties.

3D biofabrication is one of the most researched topics in the scientific community, and constant innovations are being introduced in this field. Biofabrication refers to the generation of tissues and organs through bioprinting, bioassembly, and maturation [1]. The difference between biofabrication and conventional AM is in the inclusion of cells with the manufactured biomaterials for producing so-called bio-inks. Laser-induced forward transfer (LiFT), inkjet printing, and robotic dispensing are being used for bioprinting with bio-inks. The range of materials for 3D bioprinting is very limited [59], and mainly natural polymers and bio-compatible synthetic polymers such as modified diblock copolymers, sodium alginate, chitosan, and acrylates-based polymers are being used [60,61]. Materials and technologies for 3D drug printing for the pharmaceutical industry and implant industry are also constantly in development.

One of the innovative approaches to 3D printing materials is the development of so-called digital materials, which are advanced composite materials that consist of two or more photopolymers in specific microstructures and ratios [62]. They can simulate various elastomers, mimic standard plastics, and produce photorealistic details for different kind of applications. Another approach of material innovation is through developing smart materials for 4D printing. These materials can transform their geometry under the influence of some external stimuli [63–65].

The emergence of soft active materials (SAMs) as a class of materials capable of exhibiting large elastic deformation in response to environmental stimuli such as heat, light, and electricity enables the creation of functional, active components. Shape memory polymers (SMPs), hydrogels, dielectric elastomers in integration with 3D printing opened up the new research and application field recently known as 4D printing. Printed 3D structures created with 4D printing technology can actively transform their configurations over time in response to environmental stimuli [66]. According to Ge and his associates, two types of SAMs are mainly used in 4D printing: SMPs that are capable to temporarily change their shape and recover to the permanent shape upon heating [67] and hydrogels that swell when solvent molecules diffuse into polymer network [68].

Besides the ability to temporarily change their shape, SMPs have many advantages: lightweight, low cost, highly flexible programming, good biocompatibility, and biodegradability [69]. These sets of unique characteristics made them suitable for use in biomedical devices, deployable space structures, shape-morphing structures, and microelectromechanical systems [70].

Composite materials such as PLA/Fe_3O_4 [71], PLA/CNT [72], PLA/15% Hydroxyapatite [73], tBA-co-DEGDA [74], PU/MWNT [75], (meth)acrylate resin system [76], recyclable shape memory polymer (RSMP) [77], acrylic acid cross-linked with BPA ethoxylate dimethacrylate [78], PLMC/CNT [79], and PLA/spring steel strip (SSS) [80] are examples of shape memory polymeric materials used in 4D printing mentioned in the work of Subash and Kandasubramanian [81]. Some available hydrogels are double-network (DN) systems based on poly(2-acrylamide-2-methyl propane sulfonic acid) (PAMPS) and polyacrylamide (PAAm) [82].

According to Mordor Intelligence [83], the 4D printing market is segmented by type of programmable material on programmable carbon fiber, programmable textiles, programmable biomaterial, and programmable wood. A CAGR of 41.96% in the study period from 2018 to 2026 is predicted in their report. In 2020 the 4D printing market was valued at USD 62.02 million and was expected to reach USD 488.02 million by 2026. The advancement in biofabrication is predicted to drive 4D printing in the forecast period. In the report, North America is identified to be among the lead innovators and pioneers and holds the highest share in 2020 regarding the adoption of AM and is expected to be the market leader over the forecast period. According to this report, Asia-Pacific is expected to have the highest growth rate in the 4D printing market. The market is identified to be highly competitive without any dominating players. Companies invest with the accelerated speed in research and development for 4D printing. The major companies operating in the 4D printing market are MIT Self-Assembly Lab, Autodesk Inc., Stratasys Ltd., Hewlett Packard Enterprise Company, CT CoreTechnologie Group, and EncisionTEC Inc., among the others [83], BASF SE, Cornerstone Research Group, SINOPEC, Covestro, EndoShape, Evonik, MedShape, Mitsubishi, Spintech Holdings Inc., Syzygy Memory Plastics [84], 3D systems corporation, Materialise NV, Organovo Holdings, Inc., Dassault Systems SA.

In the report of Verified market research [85], the 4D printing market size was valued at USD 87.4 million in 2020 and is projected to reach USD 737.76 million by 2028, growing at a CAGR of 30.6% from 2021 to 2028. It is expected that the need for reduction in manufacturing and process cost and the drive for a sustainable environment will lead to the rise in the market revenue of 4D printing and foster market growth. Verified market research [85] anticipated that military and defense is the largest increasing segment for 4D printing among medical, automotive, and others.

19.8 Major challenges for polymer in 3D printing

Concerning the implementation of 3D printing technology in the industry, there are numerous challenges such as high prices and investment, lack of capability, and technological limitations such as production speed, size of printed products, and product quality [86]. According to EY's Global 3D printing report, 90% of companies that participated in the survey pointed out the high cost of materials as the biggest hurdle to implementing AM in their workflow. The second hurdle represents the high cost of the systems (87% of responses) needed for industrial production. Lack of in-house knowledge of design for AM (50% of responses) and AM production processes (46% of responses) are the third and fourth challenges for implementing 3D printing. Production speed is in the fifth place (41% of responses) on the list of challenges put upon implementation of 3D printing in the production process. Next on the list is lack of knowledge to identify feasible use cases (40% of responses) followed by limitations of current systems in size of printed products (36% of responses), limitations of current systems in materials or multimaterials (21% of responses), and concerns about product quality (19% of responses).

A large part of the mentioned challenges of 3D printing, in general, can be transposed to 3D printing with polymers. Stansbury and Idacavage [2] pointed out that the recent growth of 3D printing has been dramatic, which dictates that various printing techniques need to expand from rapid production of prototypes to the greater volume of readily customizable working parts implying high growth rates. This transition requires materials that can deliver physical and mechanical properties necessary for the application alongside requisite design accuracy. Concerning photopolymer resins, there are two common challenges put upon new materials: the capability to fast cure monomers and the ability to be cured without producing warped parts. In order to achieve good mechanical properties, initiators in the monomers should be matched well to the irradiation source and have molar absorptivity to achieve high photocuring efficiency and a shallow depth of cure [2]. Jetted polymer materials require a shear-thinning, non-Newtonian fluid as a desirable component that provides some restriction in the material choice. Required constant viscosity can be achieved with either reactive diluent or heated print heads [2]. For the polymers used in the selective laser sintering (SLS) process, particle size, shape, and free packing density are critical factors in the material design and thermal behavior. Spherical particles flow more easily and pack more densely than irregular shapes, and small particles create processing difficulties due to either excessive cohesion or electrostatic repulsive forces [2]. There is also a significant influence of printing parameters on different mechanical properties associated with SLS printing, such as part orientation and dependence on process parameters on different models of printing machines. In the binder jetting technique, the choice of polymeric materials is much broader than with SLS since the requirements involved with thermal processing properties are largely avoided. However, there are apparent solvent resistance considerations due to solvent welded parts. The major challenge for the FDM 3D printing technique is reducing the anisotropy of printed parts. One solution to this problem is introducing ionizing radiation that provides a route to convert a thermoplastic polymer to a thermoset printed part with more homogenous mechanical properties and greater solvent resistance. Thermal postprint treatment and well-designed parts can also contribute to printed parts with reduced anisotropic character [2]. According to the authors, factors such as material costs, production speed and volume, energy costs, properties, lifetimes, and recycling potential of printed parts represent challenges for polymer 3D printing.

19.9 Conclusions

3D printing techniques are designed and continuously improved to be able to process a specific category of ever-developing materials on the market and to satisfy the most diverse needs of today's end-users. There are many different estimations of the size and the value of 3D printing materials market and predictions about further changes, but it can be concluded that this market is growing and developing in significant pace to accommodate demands of manufacturers as well as products consumers. There is still a certain degree of limitations in the aspect of available materials, their mechanical, thermal, physical, and chemical properties, and their costs, but it is rapidly dissolving with every research done in this field. The compound annual growth rate of the 3D printing market, as well as printing materials in the recent period, is recorded to be between 20% and 30% across different market reports which represents one of the indications of the industry worth of further development and improvement. Photopolymers have a larger market share compared to other polymer materials followed by thermoplastic polymers. PA has the highest growth rate, and it is mostly used in powder bed fusion 3D printing technique. Also, due to the decline in desktop 3D printers prices, especially FDM technique, there is an increased demand for thermoplastic filament form of material which represents a fertile ground for the proliferation of many filament manufacturers. With ever-growing market demands and need to substitute or at least supplement traditional manufacturing techniques, 3D printing materials need to meet specific requirements. Much of the work toward these goals are done in the plastics segment by developing different polymer combinations and by introducing other material particles in the polymeric matrix. This leads to the manufacturing of different kinds of composite materials with improved or added values. Another goal of material development and development of 3D printing techniques, in general, should be in implementing sustainability principles throughout the whole life cycle of a product, so harm done to our environment and health would be significantly reduced. Use of bio-based and biodegradable polymers is just one step closer to that goal.

References

[1] T.D. Ngo, A. Kashani, G. Imbalzano, K.T. Nguyen, Additive manufacturing (3D printing): a review of materials, methods, applications and challenges, Compos. B Eng. 143 (2018) 172–196.

[2] J.W. Stansbury, M.J. Idacavage, 3D printing with polymers: challenges among expanding options and opportunities, Dent. Mater. 32 (1) (2016) 54–64.

[3] S.A. Tofail, E.P. Koumoulos, A. Bandyopadhyay, S. Bose, L. O'Donoghue, C. Charitidis, Additive manufacturing: scientific and technological challenges, market uptake and opportunities, Mater. Today 21 (1) (2018) 22–37.

[4] BCC Research, Market Research Reports. Instruments. IAS102B. Global Markets for 3D Printing, 2016. https://www.bccresearch.com/market-research/instrumentation-and-sensors/3d-printing-global-markets-report-ias102b.html (Accessed 21 June 2019).

[5] BCC Research, Market Research Reports. Instruments. IAS118B. Educational Equipment and Software: Global Markets, 2017. https://www.bccresearch.com/market-research/instrumentation-and-sensors/educational-equipment-and-software-global-markets.html (Accessed 21 June 2019).

[6] BCC Research, Market Research Reports. Instruments. IAS102C. Global Markets for 3D Printing, 2018. https://www.bccresearch.com/market-research/instrumentation-and-sensors/global-markets-for-3d-printing.html (Accessed 21 June 2019).

[7] B.M. Oviatt, P.P. McDougall, Toward a theory of international new ventures, J. Int. Bus. Stud. 25 (1) (1994) 45–64.

[8] M.E. Porter, Competitive Advantage – Creating and Sustaining Superior Performance, The Free Press, New York, NY, 1985.

[9] METI, METI White Paper Year 2001, 2002. http://www.meti.go.jp/english/report/index.html (Accessed 14 July 2019).

[10] WTO World Trade Organization, International Trade Statistics 2013, 2013. http://www.wto.org/statistics (Accessed 17 July 2019).

[11] S. Globerman, T.W. Roehl, S. Standifird, Globalization and electronic commerce: inferences from retail brokering, J. Int. Bus. Stud. 32 (4) (2001) 749–768.

[12] N. Hopkinson, R. Hague, P. Dickens (Eds.), Rapid Manufacturing: An Industrial Revolution for the Digital Age, John Wiley & Sons, Chichester, 2006.

[13] N. Gershenfeld, Fab: The Coming Revolution on Your Desktop-From Personal Computers to Personal Fabrication, Basic Books, New York, NY, 2008.

[14] H. Lipson, M. Kurman, Fabricated: The New World of 3D Printing, John Wiley & Sons, Chichester, 2013.

[15] J. Moilanen, T. Vadén, 3D printing community and emerging practices of peer production, Clin. Hemorheol. and Microcirc. 18 (8) (2013).

[16] A.O. Laplume, B. Petersen, J.M. Pearce, Global value chains from a 3D printing, J. Int. Bus. Stud. 47 (5) (2016) 595–609.

[17] P. Ghemawat, World 3.0 – Global Prosperity and How to Achieve it, Harvard Business Review Press, Boston, MA, 2011.

[18] H.J. Nyman, P. Sarlin, From bits to atoms: 3D printing in the context of supply chain strategies, in: 2014 47th Hawaii International Conference on System Sciences. Waikoloa, HI, USA, January 6–9, 2014, 2013, pp. 4190–4199.

[19] A. Ben-Ner, E. Siemsen, Decentralization and localization of production: the organizational and economic consequences of additive manufacturing (3D printing), Calif. Manag. Rev. 59 (2) (2017) 5–23.

[20] Sculpteo, The State of 3D Printing 2019, 2019. https://www.sculpteo.com/blog/2019/05/29/download-your-state-of-3d-printing-for-free/ (Accessed 09 August 2019).

[21] Sculpteo, Online 3D Printing Service, 2019. https://www.sculpteo.com/en/3d-printing/ (Accessed 07 September 2019).

[22] Sculpteo, The State of 3D Printing 2020, 2020. https://info.sculpteo.com/hubfs/downloads/The%20State%20of%203D%20Printing_2020%20edition.pdf (Accessed 09 August 2019).

[23] M.D. Monzón, Z. Ortega, A. Martínez, F. Ortega, Standardization in additive manufacturing: activities carried out by international organizations and projects, Int. J. Adv. Manuf. Technol. 76 (5–8) (2015) 1111–1121.

[24] E. Anderson, Additive Manufacturing in China: Threats, Opportunities and Developments (Part 1), 2013. https://escholarship.org/uc/item/9x38n9b3 (Accessed 10 June 2019).

[25] R. Gordon, 3D Printing Materials Markets: 2014–2025 -Trends, Key Players and Forecasts, 2015. https://www.3dprintingmaterialsconference.com/wp-content/uploads/2015/02/Rachel-Gordon-IDTechEx.pdf (Accessed 18 August 2019).

[26] O. Jurevicius, BCG Growth-Share Matrix, 2013. https://www.strategicmanagementinsight.com/tools/bcg-matrixgrowth-share.html (Accessed 23 August 2019).

[27] Wohlers Associates, Wohlers Report 2017. 3D Printing and Additive Manufacturing State of Industry, Annual Worldwide Progress Report, 2017. https://www.wohlersassociates.com/2017report.htm (Accessed 3 September 2019).

[28] Wohlers Associates, Wohlers Report 2018. 3D Printing and Additive Manufacturing State of Industry, Annual Worldwide Progress Report, 2018. http://www.wohlersassociates.com/2018report.htm (Accessed 8 September 2019).

[29] MarketsandMarkets Research Private Ltd, Top Markets Reports. 3D Printing Market with COVID-19 Impact Analysis by Offering (Printer, Material, Software, Service), Process (Binder Jetting, Direct Energy Deposition, Material Extrusion, Material Jetting, Powder Bed Fusion), Application, Vertical, Technology, and Geography - Global Forecast to 2026, MarketsAndMarkets, 2017. https://www.marketsandmarkets.com/Market-Reports/3d-printing-market-1276.html (Accessed 25 August 2019).

[30] Prescient & Strategic Intelligence, Semiconductor and Electronics. 3D Printing Market, 3D Printing Market by Components (Printer [Industrial Printer, Desktop 3D Printer], Material [Metals, Polymers, Ceramics], Software [Design Software, Printer Software, Scanning Software, Inspection Software], Service [Custom Design & Manufacturing, After-Sales Services], by Process (Powder Bed Fusion, Binder Jetting, Direct Energy Deposition, Sheet Lamination, Vat Photopolymerization, Material Extrusion, Material Jetting), by Technology, by Application, by Industry, by Geography (U.S., Canada, Germany, U.K., Italy, Spain, Japan, China, India, South Africa, Mexico, Brazil) – Global Market Size, Share, Development, Growth, and Demand Forecast, 2013–2023, 2018. https://www.psmarketresearch.com/market-analysis/3d-printing-market (Accessed 15 August 2019).

[31] ASTM International, ISO/ASTM 52900:2015 [ASTM F2792] Additive Manufacturing — General Principles—Terminology, 2015.

[32] B. Core, 3D Printing Materials 2019–2029: Technology and Market Analysis: Current and Future Technologies, and Market Forecasts, 2019. https://www.idtechex.com/de/research-report/3d-printing-materials-2019-2029-technology-and-market-analysis/668 (Accessed 22 August 2019).

[33] Markets and Markets Research Private Ltd, 3D Printing Materials Market, 2018. https://www.marketsandmarkets.com/PressReleases/3d-printing-materials.asp (Accessed 28 August 2019).

[34] Wohlers Associates, Wohlers Report 2019, 2019. https://wohlersassociates.com/2019report.htm (Accessed 10 September 2019).

[35] SmarTech Analysis, 2019 Additive Manufacturing Market Outlook and Summary of Opportunities, 2018. https://3dprint.com/231944/smartech-publishing-releases-year-end-am-market-review/ (Accessed 20 August 2019).

[36] M. Schmid, K. Wegener, Additive manufacturing: polymers applicable for laser sintering (LS), Procedia Eng. 149 (2016) 457–464.

[37] Grand View Research, 3D Printing Plastics Market Size, Share & Trends Analysis Report by Type (ABS & ASA, Photopolymers, Polyamide/Nylon, PLA), by Form (Filament, Ink, Powder), by Application, and Segment Forecasts, 2018–2025 (Historical Data: 2014–2016, Year of Estimation 2017), 2018. https://www.grandviewresearch.com/industry-analysis/3d-printing-plastics-market (Accessed 15 August 2019).

[38] Markets and Markets Research Private Ltd, 3D Printing Plastics Market by Type (Photo Polymer, ABS, Polyamide, PLA), Form (Filament, Liquid/Ink, Powder), End-Use Industry (Healthcare, Aerospace & Defense, Automotive, Electrical & Electronics), Application, and Region – Global Forecast to 2023, 2018. https://www.prnewswire.com/news-releases/3d-printing-plastics-market-1-965-3-million-by-2023-814775846.html (Accessed 16 August 2019).

[39] Report consultant, Global 3D Printing Polymer Materials Market Professional Survey Report, 2019. https://www.reportconsultant.com/reports/Global-3D-Printing-Polymer-Materials-Market-Professional-Survey-Report-2019-6457 (Accessed 18 August 2019).

[40] SmarTech Analysis, Opportunities in Polymer and Plastic 3D Printing – 2017: An Opportunity Analysis And-Ten-Year Forecast, 2017. https://www.smartechanalysis.com/news/polymers-3d-printing-2022/ (Accessed 13 September 2019).

[41] S. Singh, S. Ramakrishna, R. Singh, Material issues in additive manufacturing: a review, J. Manuf. Process. 25 (2017) 185–200.

[42] 3D Hubs, Online 3D Printing Service, 2019. https://www.3dhubs.com/3d-printing/ (Accessed 07 September 2019).

[43] 3D Printing.com, 3D Printing Service, 2019. https://3dprinting.com/3d-printing-service/ (Accessed 07 Sepetember 2019).

[44] i. materialise, 3D Printing Technologies, 2019. https://i.materialise.com/en/3d-printing-technologies (Accessed 07 September 2019).

[45] JawsTec, 3D Printing Capabilities, 2019. https://www.jawstec.com/3d-printing-capabilities/ (Accessed 07 September 2019).

[46] Makexyz, 3D Printing Service on Demand, 2019. https://www.makexyz.com/ (Accessed 07 September 19).

[47] Protolabs, Manufacturing Services, 2019. https://www.protolabs.com/services/ (Accessed 07 September 2019).

[48] Shapeways, Additive Manufacturing Services by Shapeways, 2019. https://business.shapeways.com/partnership (Accessed 7 September 2019).

[49] Xometry, Manufacturing on Demand, 2019. https://www.xometry.com/ (Accessed 07 September 2019).

[50] R. Chinthapalli, P. Skoczinski, M. Carus, W. Baltus, D. de Guzman, H. Käb, et al., Biobased building blocks and polymers—global capacities, production and trends, 2018–2023, Ind. Biotechnol. 15 (4) (2019) 237–241.

[51] F. Aeschelmann, M. Carus, Bio-based Building Blocks and Polymers in the World. Capacities, Production and Applications: Status Quo and Trends towards, vol. 2020, nova-Institute GmbH, 2015, pp. 1–23.

[52] P. Skoczinski, M. Carus, D. de Guzman, H. Käb, R. Chinthapalli, J. Ravenstijn, et al., Bio-Based Building Blocks and Polymers – Global Capacities, Production and Trends 2020–2025, Nova-Institut GmbH, 2021. https://renewable-carbon.eu/publications/product/bio-based-building-blocks-and-polymers-global-capacities-production-and-trends-2020-2025-graphics-figure-1-png/ (Accessed 11 July 2021).

[53] F.A. Kucherov, E.G. Gordeev, A.S. Kashin, V.P. Ananikov, Three-dimensional printing with biomass-derived PEF for carbon-neutral manufacturing, Angew. Chem. Int. Ed. 56 (50) (2017) 15931–15935.

[54] J. Pakkanen, D. Manfredi, P. Minetola, L. Iuliano, About the use of recycled or biodegradable filaments for sustainability of 3D printing, in: International Conference on Sustainable Design and Manufacturing, Bologna, Italy April 26–28, 2017, 2017, pp. 776–785.

[55] C.C. Kuo, L.C. Liu, W.F. Teng, H.Y. Chang, F.M. Chien, S.J. Liao, et al., Preparation of starch/acrylonitrile-butadiene-styrene copolymers (ABS) biomass alloys and their feasible evaluation for 3D printing applications, Compos. B Eng. 86 (2016) 36–39.

[56] M. Ceccolini, AgriDust – Biodegradable Material, 2015. https://www.behance.net/gallery/24616719/agridustbiodegradable-material (Accessed 09 July 2019).

[57] S3D Innovations, Renewable Soy based Filament for your 3D printer. https://s3dinnovations.wixsite.com/filasoy (Accessed 12 July 2019).

[58] D. Zhang, B. Chi, B. Li, Z. Gao, Y. Du, J. Guo, et al., Fabrication of highly conductive graphene flexible circuits by 3D printing, Synth. Met. 217 (2016) 79–86.

[59] Biomaterials and bioprinting [special issue], in: C. Chua, W. Yeong, J. An (Eds.), Molecules 21 (9) (2016).

[60] B. Derby, Printing and prototyping of tissues and scaffolds, Science 338 (6109) (2012) 921–926.

[61] W.L. Ng, W.Y. Yeong, M.W. Naing, Polyelectrolyte gelatin-chitosan hydrogel optimized for 3D bioprinting in skin tissue engineering, Int. J. Bioprint. 2 (1) (2016) 53–62.

[62] J.Y. Lee, J. An, C.K. Chua, Fundamentals and applications of 3D printing for novel materials, Appl. Mater. Today 7 (2017) 120–133.

[63] J. An, C.K. Chua, V. Mironov, A perspective on 4D bioprinting, Int. J. Bioprint. 2 (1) (2016) 3–5.

[64] Z.X. Khoo, J.E.M. Teoh, Y. Liu, C.K. Chua, S. Yang, J. An, et al., 3D printing of smart materials: a review on recent progresses in 4D printing, Virtual Phys. Prototyp. 10 (3) (2015) 103–122.

[65] S.K. Leist, J. Zhou, Current status of 4D printing technology and the potential of light-reactive smart materials as 4D printable materials, Virtual Phys. Prototyp. 11 (4) (2016) 249–262.

[66] Q. Ge, A.H. Sakhaei, H. Lee, C.K. Dunn, N.X. Fang, M.L. Dunn, Multimaterial 4D printing with tailorable shape memory polymers, Sci. Rep. 6 (1) (2016) 1–11.

[67] H. Meng, G. Li, A review of stimuli-responsive shape memory polymer composites, Polymer 54 (9) (2013) 2199–2221.

[68] D. Raviv, W. Zhao, C. McKnelly, A. Papadopoulou, A. Kadambi, B. Shi, et al., Active printed materials for complex self-evolving deformations, Sci. Rep. 4 (1) (2014) 1–8.

[69] M. Bodaghi, A.R. Damanpack, W.H. Liao, Triple shape memory polymers by 4D printing, Smart Mater. Struct. 27 (6) (2018) 065010.

[70] Y. Liu, H. Du, L. Liu, J. Leng, Shape memory polymers and their composites in aerospace applications: a review, Smart Mater. Struct. 23 (2) (2014) 023001.

[71] F. Zhang, L. Wang, Z. Zheng, Y. Liu, J. Leng, Magnetic programming of 4D printed shape memory composite structures, Compos. Appl. Sci. Manuf. 125 (2019) 105571.

[72] Y. Liu, W. Zhang, F. Zhang, J. Leng, S. Pei, L. Wang, et al., Microstructural design for enhanced shape memory behavior of 4D printed composites based on carbon nanotube/polylactic acid filament, Compos. Sci. Technol. 181 (2019b) 107692.

[73] F.S. Senatov, K.V. Niaza, M.Y. Zadorozhnyy, A.V. Maksimkin, S.D. Kaloshkin, Y.Z. Estrin, Mechanical properties and shape memory effect of 3D-printed PLA-based porous scaffolds, J. Mech. Behav. Biomed. Mater. 57 (2016) 139–148.

[74] Y.Y.C. Choong, S. Maleksaeedi, H. Eng, S. Yu, J. Wei, P.C. Su, High speed 4D printing of shape memory polymers with nanosilica, Appl. Mater. Today 18 (2020) 100515.

[75] S.T. Ly, J.Y. Kim, 4D printing–fused deposition modeling printing with thermal-responsive shape memory polymers, Int. J. Precis. Eng. Manuf. - Green Technol. 4 (3) (2017) 267–272.

[76] J.T. Miao, M. Ge, S. Peng, J. Zhong, Y. Li, Z. Weng, et al., Dynamic imine bond-based shape memory polymers with permanent shape reconfigurability for 4D printing, ACS Appl. Mater. Interfaces 11 (43) (2019) 40642–40651.

[77] A. Li, A. Challapalli, G. Li, 4D printing of recyclable lightweight architectures using high recovery stress shape memory polymer, Sci. Rep. 9 (1) (2019) 1−13.

[78] C. Yang, M. Boorugu, A. Dopp, J. Ren, R. Martin, D. Han, et al., 4D printing reconfigurable, deployable and mechanically tunable metamaterials, Mater. Horiz. 6 (6) (2019) 1244−1250.

[79] X. Wan, F. Zhang, Y. Liu, J. Leng, CNT-based electro-responsive shape memory functionalized 3D printed nanocomposites for liquid sensors, Carbon 155 (2019) 77−87.

[80] Y. Liu, F. Zhang, J. Leng, L. Wang, C. Cotton, B. Sun, T.W. Chou, Synergistic effect enhanced shape recovery behavior of metal-4D printed shape memory polymer hybrid composites, Compos. B Eng. 179 (2019a) 107536.

[81] A. Subash, B. Kandasubramanian, 4D printing of shape memory polymers, Eur. Polym. J. 134 (2020) 109771.

[82] S. Naficy, G.M. Spinks, G.G. Wallace, Thin, tough, pH-sensitive hydrogel films with rapid load recovery, ACS Appl. Mater. Interfaces 6 (6) (2014) 4109−4114.

[83] Mordor Intelligence, 4D Printing Market − Growth, Trends, COVID-19 Impact, and Forecasts (2021−2026), 2020. https://www.mordorintelligence.com/industry-reports/4d-printing-market (Accessed 10 July 2021).

[84] The Courier, Global 4D Printing Materials Market 2021 to 2026 − Qualitative and Quantitative Assessment by Industry Analysis across the Value Chain, 2021. https://www.mccourier.com/global-4d-printing-materials-market-2021-to-2026-qualitative-and-quantitative-assessment-by-industry-analysis-across-the-value-chain/ (Accessed 14 July 2021).

[85] Verified market research, Global 4D Printing Market Size By Material (Programmable Carbon Fiber, Programmable Wood-Custom Printed Wood Grain, Programmable Textile), By End User (Medical, Aerospace and Defense, Automotive), By Geographic Scope And Forecast, 2021. https://www.verifiedmarketresearch.com/product/4d-printing-market/ (Accessed 12 July 2021).

[86] EY, 3D Printing: Hype or Game Changer? A Global EY Report 2019, 2019. https://assets.ey.com/content/dam/ey-sites/ey-com/en_gl/topics/advisory/ey-3d-printing-game-changer.pdf (Accessed 13 July 2021).

CHAPTER

20

3D printing trends and perspectives

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20.1 Introduction

Human kind has often created scenarios, in fictional universes of books and films, in which machines would dominate the world, often becoming enemies of man himself. However, when the imaginary became reality, things were — and still are — very different. It seems that the “3D Printer Revolution” has rised to help and transform people’s reality by making it much easier and more creative. Life built in layers is now present in education, whether for children or university students, in medicine, in civil construction, in the houseware, furniture, and decoration of houses, in clothes, in food, and in most of what is necessary for the “Human machine” to work.

Much of the development, and consequently the success, of 3D printing is related to, or based on, polymeric materials. Polymers, due to its low processing temperatures, density, price, and easy processability, continue to dictate the main trends in this technological environment, which are the object of study in this chapter. To guide this investigation, we carried out a mapping using Publish or Perish 7 software and Word Clouds to analyze the main keywords found in the last 1000 paper titles indexed in Google Scholar, between 2019 and 2020, using as input the expression “3D printing polymers.”

This first stage was characterized by a bibliometric analysis, with which, in addition to the titles of publications, it was also possible to obtain its abstracts. All information found, titles and abstracts, was broken down into words, used to build the cloud of Fig. 20.1. The word cloud provides a visual analysis of the most and least relevant terms, or occurrences, found in the literature scan.

After the first scan, we treated the data obtained in a second stage through an analysis of ontologies, in which we grouped terms according to an idea, or global concept, that relates them. In addition, obvious words common to all groups (3D printing, material, layer, etc.) were discarded from the raw data. With this, we defined five central elements to be approached (Fig. 20.2) following a day-to-day base: construction industry (where we live), food (what we eat), bio (when we are treated), composites (tools that might help), and smart polymers (the future). The “Word Clouds” platform also informs how many times a word is mentioned. These values were used to determine the percentages associated with each group (ontologies) in Fig. 20.2.

A quantitative analysis and a visual representation of the most recurrent words found in bibliometrics delimit a scientific/technological moment associated with polymer-based 3D printing. The logic is similar to that of the “trending topics,” which register a moment of relevance of the subjects on social networks, albeit ephemeral. In the future, scientific advances are transposed to the market (companies, industrialists) and consumers. Thus, initially, trends are captured in this chapter, represented by the five main groups mentioned above. The breakdown of these groups defines the perspectives of the subjects based on the knowledge described by different authors in the literature, which will be done in the following topics.

Polymers for 3D Printing
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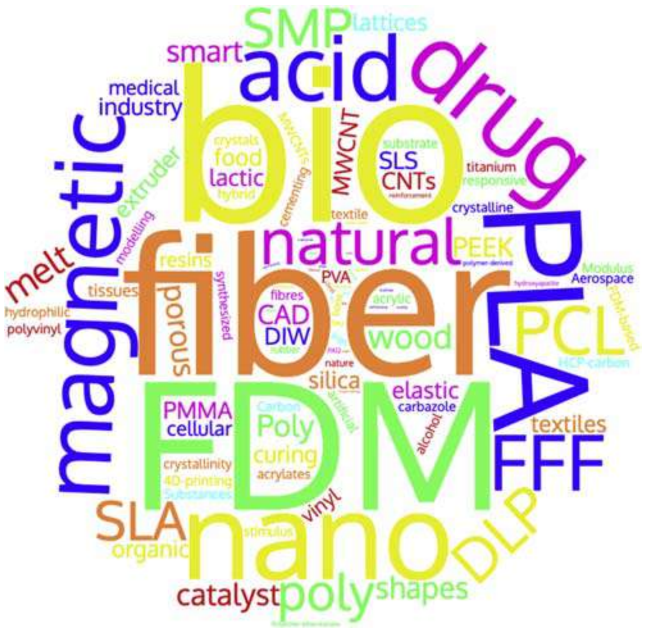

FIGURE 20.1 Word Cloud with terms obtained from the bibliometric analysis. (Source: *the Authors*).

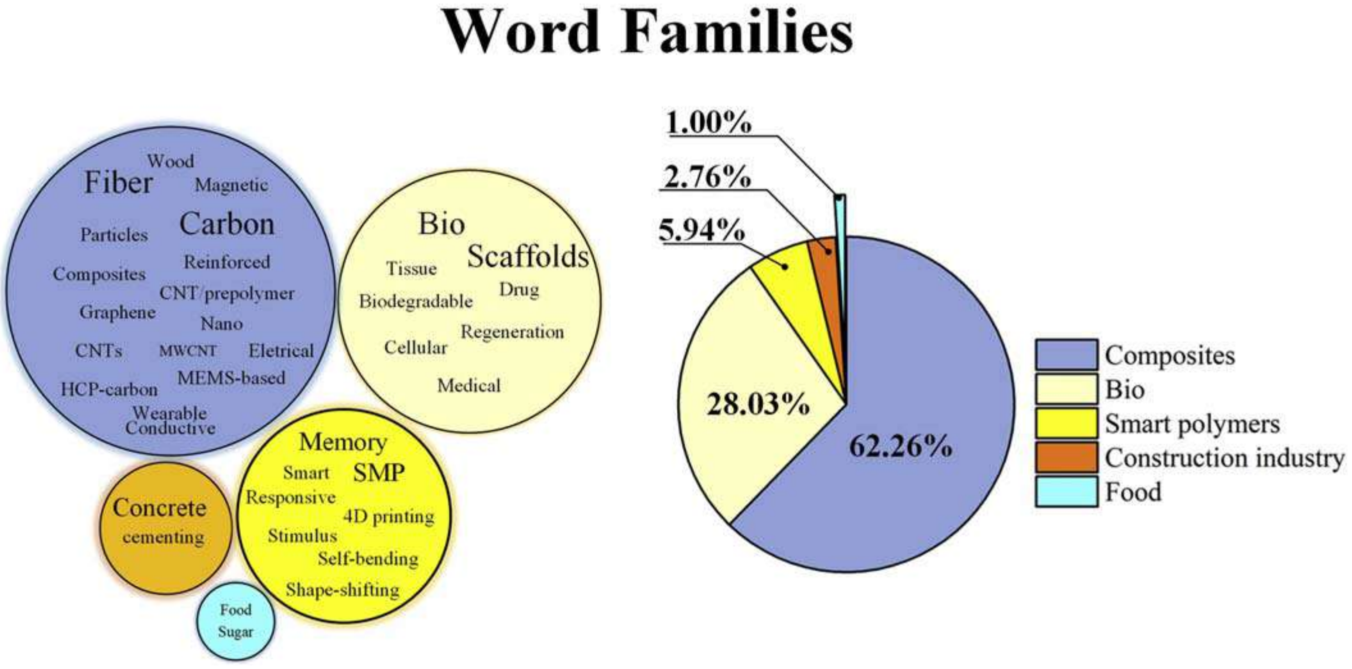

FIGURE 20.2 Elements, or families, for the analysis. (Source: *the Authors*).

20.2 Construction industry

Let's start approaching the trends in 3D printing by presenting solutions that might be used to build houses, buildings, warehouses, urban furniture, and more. Constructions, as we have traditionally known them, generally have their fundamental structures based on materials such as concrete (sand, stone, cement, and water, among others), metals, and wood. How would this work in additive manufacturing (AM) with polymeric materials? That is what we try to answer in this topic.

Polymeric concretes (PCs) appear in the literature as a good solution to 3D printing. In general, these can be found in three types: (1) in the replacement of traditional cement binders in concrete with polymeric binders, such as liquid resins; (2) in latex-modified concrete, such as Styrene-Butadiene Rubber (SBR); and (3) as an impregnating agent that is used to impregnate a hardened porous concrete that will then be submitted to a polymerization process by temperature or radiation [1]. Within the extrusion-based AM scenario, Taha et al. [1] point out that the establishment of PCs will depend on a series of studies in flowability, extrudability, open time, and buildability. These factors add rheological and adhesion characteristics, and determine possible the number of layers to be built without collapsing.

Considering materials formulation, there are studies like the one from Yeon et al. [2,3] which evaluated EVA (Ethylene-Vinyl Acetate) and cement composites, demonstrating the effects of the ratio between these components on the variation of the four factors mentioned above and the mechanical properties − compression and flexion − of parts manufactured with these mixtures by the extrusion-based 3D printing process. Both works attest, given the best fit, the feasibility of using the compound for this technology. Similar analyses are described by Kim et al. [4,5] with the addition of a different polymer to the cement, an SBR. The results obtained show that the fluidity of the material, the extrusion capability, and open time increase as the SBR/cement ratio grows. In addition, in the highest proportion of SBR tested in the mixture, the resistance to compression and flexion, in comparison with the material without it, and for a curing time of 28 days, increased from 35.63 to 43.64 MPa and from 11.97 to 14.86 MPa, respectively.

Polymeric materials can also be used as a direct strategy for improving adhesion between consecutive layers of extruded concrete. The poor adhesion, according to Hosseini et al. [6], is one of the major barriers to the use of the technique in this scenario. The authors propose the application of an intermediate layer as a solution, that is, between two concrete layers, based on mortar, containing a synthesized polymer (SBC) from sulfur (99%) and black carbon (1%). Samples with this arrangement presented a tensile strength in the region between layers of approximately double (1.5 MPa) than that achieved in a concrete/concrete joint (0.75 MPa). Such improvement is due to a series of benefits of the composite, ranging from increased chemical interaction, formation of a moisture barrier, and filling of pores, among others. For the researchers, the use of sulfur as the main ingredient makes the composite ecological, since it can use residues at a low cost compared to other adhesive solutions.

Another way of using polymers in 3D printing for the construction industry can go beyond the actual production of a material, but rather in the combination of structures in different materials. It is what Furet et al. [7] did when proposing the Batiprint3d™ system. It consists in the use of a mobile and polyarticulated robot for the development of a complex wall formed by two walls of a polymeric foam (Polyurethane, PU) with a concrete center. According to the authors, with this method it is possible to aggregate all the necessary structural and thermal insulation parts with a single device. The foam walls are submitted to a finishing process, which consists of covering the outside with a classic mortar, aiming at protection from the weather, and the inside with plasterboard, to provide resistance to flammability.

In September 2017, the technique was tested in the field by building a life-size project: Yhnova™ (Figs. 20.3 and 20.4). The manufactured housing, located in the city of Nantes (France), has a built area of 95 m^2, with four bedrooms and a living room, and took 54 h to print [7].

Despite being a utopian plan, the companies Emerging Objects and Bold Machines showed how it is possible to manufacture a house, similar to an Igloo, entirely built with modules printed in poly(lactic acid) (PLA). The "Star Lounge" project consists of 2073 hexagonal blocks produced with the aid of a farm with more than 100 desktop-type 3D printers [8,9] (Fig. 20.5).

In the book *Printing Architecture: Innovative Recipes for 3D Printing* [9], Ronald Rael and Virginia San Fratello of Emerging Objects describe a series of application cases in construction using salt, wood powder, rubber, sand, and cement, using polymeric binders and natural materials. Most of the referred projects are based on modules, printed on desktop printers or printers with small building envelopes, which are then assembled to obtain big objects − "Turning the small into the big." There is also the example called Saltygloo. It is made of "salt y glue" − a combination of salt harvested from the San Francisco Bay and glue derived from natural materials.

3D printing is not only changing buildings themselves, but also furniture and pieces of decoration. Tiny particles that come from sanding or cutting wood (sawdust) were mixed with pulverized walnut shells and powder-based glues activated by water, to 3D print a Sawdust screen tiles that are affixed together to form a variably dimensional enclosure and surface. The rubber pouf is a playful piece of furniture, printed in eight parts, made with 50 mm rubber particles mixed with an organic binder. The 3D-printed earthscrapers are made of sand mixed with an organic binder, causing the particles to stick together to form a new kind of sandstone. These earthscrapers were exhibited at 2010 Biennial of the Americas, where the authors claim a landscape where the earth is architecture, and the

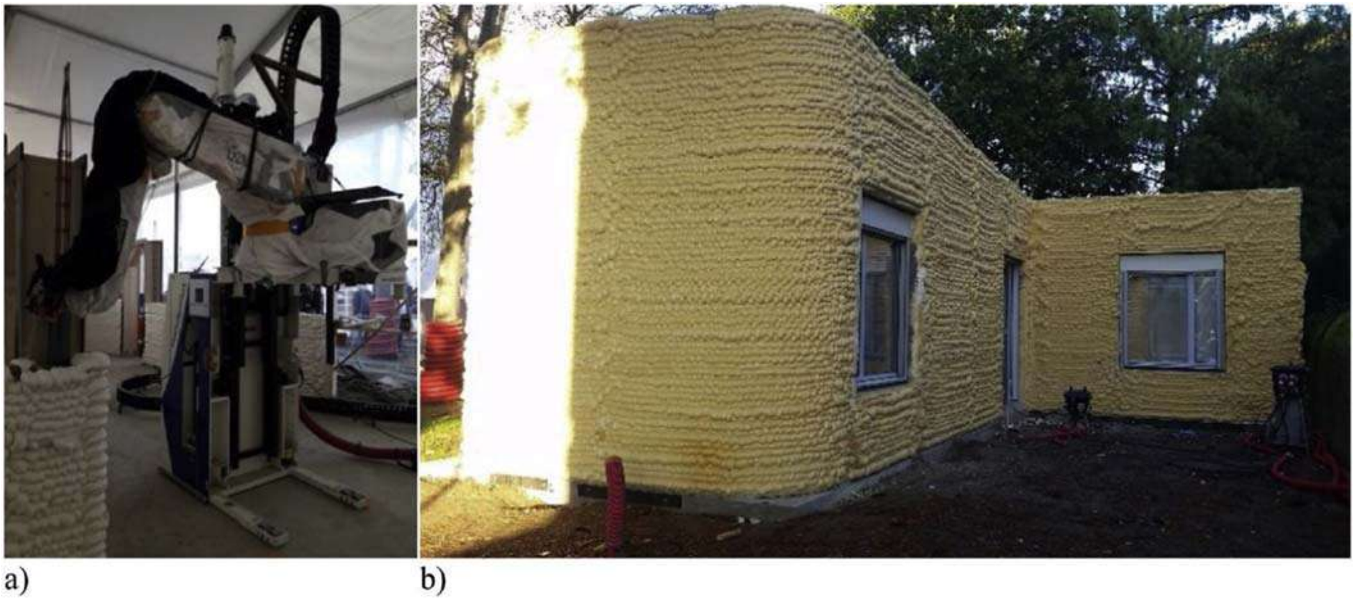

FIGURE 20.3 A) Robots at work (AGV + PAA); (B) Picture of Yhnova™ without coating [7]. *Reprinted from [7], Copyright (2019), with permission from Elsevier.*

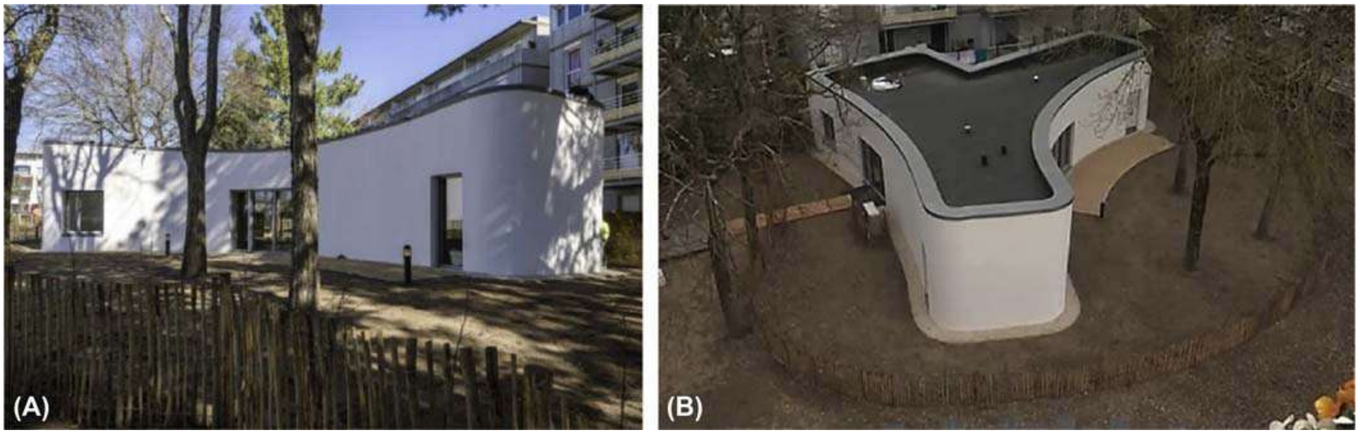

FIGURE 20.4 A) The finished social housing; (B) Yhnova™ in its environment [7]. *Reprinted from [7], Copyright (2019), with permission from Elsevier.*

architecture is earth. The Seat Slug is a biomorphic interpretation of a bench, inspired on the most recent species of sea slugs discovered off the coast of California, and by the infinite tessellations of Japanese Karakusa patterns. The result is 230 unique 3D-printed cement blocks that are coated with organic resins to create a reflective finished surface.

The growing demand for personalized products, with complex and contemporary geometries, has led architects and designers to work with the generative system. This system is based on algorithms that allow the interaction of parameters, which generate countless results based on the same formal language. Zaha Hadid (1950–2016) was the first woman to win the Pritzker Prize (considered the Nobel Prize for architecture). Her projects, with deconstructivist curves, had a great influence on architecture and contemporary design. An analysis of her works and content shows that her ideas are based on five pillars: location, art, nature, architecture, and generative software, the latter used as inspiration to generate projects, topographic contours, dunes, sedimentology, sea creatures, and living organisms [10].

FIGURE 20.5 "Star Lounge" project (photo credit: Matthew Millman Photography, courtesy of Emerging Objects). *Reprinted with permission from Ronald Rael, from Emerging Objects.*

FIGURE 20.6 3D-printed furniture models [10]. *Reprinted from [10], Copyright (2020), with permission from CIE – Comunicação e Imprensa Especializada, Lda.*

Camargo et al. [10,11] used a generative design software (Rhinoceros + Grasshopper) to reproduce the organic shape of an Amazonian tree (Carapanaúba). This geometry is applied in new furniture design (Fig. 20.6). The concept is innovative for allowing a disruptive design, where the designer can generate numerous variables of the same geometries, thus adding an exclusive value to each conceived piece.

The prototypes were printed at a 1:5 scale, using a black PLA filament of 1.75 mm in diameter. The goal is now using the extrusion technology by FGF (Fused Granular Fabrication) on a large volume printer. To finish this topic, we propose a reflection about the use of cellular geometries in the development of structures of our daily lives. Carneiro [12] and Carneiro et al. [13] suggest using extrusion-based 3D printing to build cellular structures on PLA used as intermediate model to manufacture metallic parts by investiment casting (Fig. 20.7). This is a classic example of the indirect application of AM. Such elements could be utilized in rail transportation to minimize the amount of material in its components and to provide good advantages in terms of mechanical and acoustic properties.

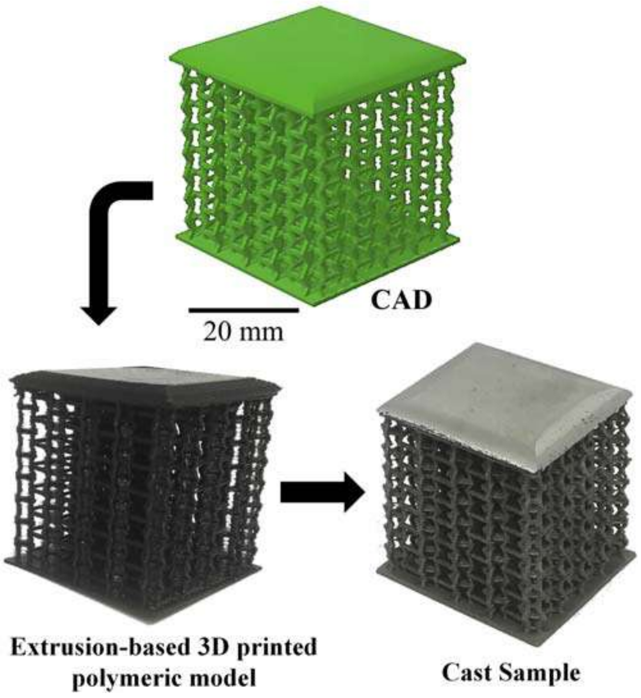

FIGURE 20.7 Metallic cellular structure built from 3D-printed polymeric models. (Source: *courtesy of Doctor Vitor Hugo Pimenta Carneiro). Printed with the author's permission.*

20.3 Food

To start this topic, it is important to mention that polymers are much more than thermoplastics or thermosets and, therefore, their insertion in the food 3D printing scenario does not imply eating steaks or plastic breads, or pasta in resin sauce.

Food polymers are used in systems that contain proteins, polysaccharides, and peptides. They are basically classified in three groups: (1) plant-based food polymers, such as starch and cereals proteins, (2) of animal origin, for example, the protein of meals, and (3) of microorganisms, such as fungal polysaccharides [14].

Hydrogels based on natural polymers are one of the most common types of materials used in food 3D printing. In this context, long chain polymers − hydrocolloids, such as cellulose derivatives, carrageenan, xanthan gum, and starch, with the ability to form viscous elements and/or gels when dispersed in water—are applied to nonprintable raw materials. They give construction stability to traditional foods to the daily lives of many people like rice, meat, fruits, and vegetables [15−18]. Several research studies show different ways of producing printable gels from the combination of products such as: soy, gelatin, and sodium alginate [19]; egg white protein, gelatin, cornstarch, and sucrose [20]; or milk protein in sodium caseinate solution [21].

Literature shows a "feast" of studies on gels with different flavors, from lemon juice [22] to cookies [23], fish [24], broccoli, spinach, and carrot [25]. Dick, Bhandari, and Prakash [26], for instance, use a double extruder head system to evaluate "parts" built from a lean meat paste, varying filling densities and the amount of fat layers (lard) in the structure (Fig. 20.8). In another case, a processed cheese was used, whose structure is basically fat, carbohydrate, protein, and salt [27], being the first three components part of the group of biological (natural) polymers [28−30].

What makes these studies even more interesting is how they manage to transform what for many could be a futuristic or enthusiastic scenario, in a reality in which 3D printing unites the art of gastronomy and engineering into a scientific project, rich in technical information and measurable. Just as in the characterization of conventional polymers (thermoplastics, for example) and the parts produced with them, the products of food 3D printing, as those evaluated in the studies above, are submitted to rheological, parametric, mechanical, friction, dimensional and geometric, color variation, and microscopic analysis, among others. In addition, parameters related to cooking, such as loss of cooking, retention of moisture and fat, contraction, and the final texture (hardness, chewability) of the products, are also targets for studies, as highlighted in Ref. [26].

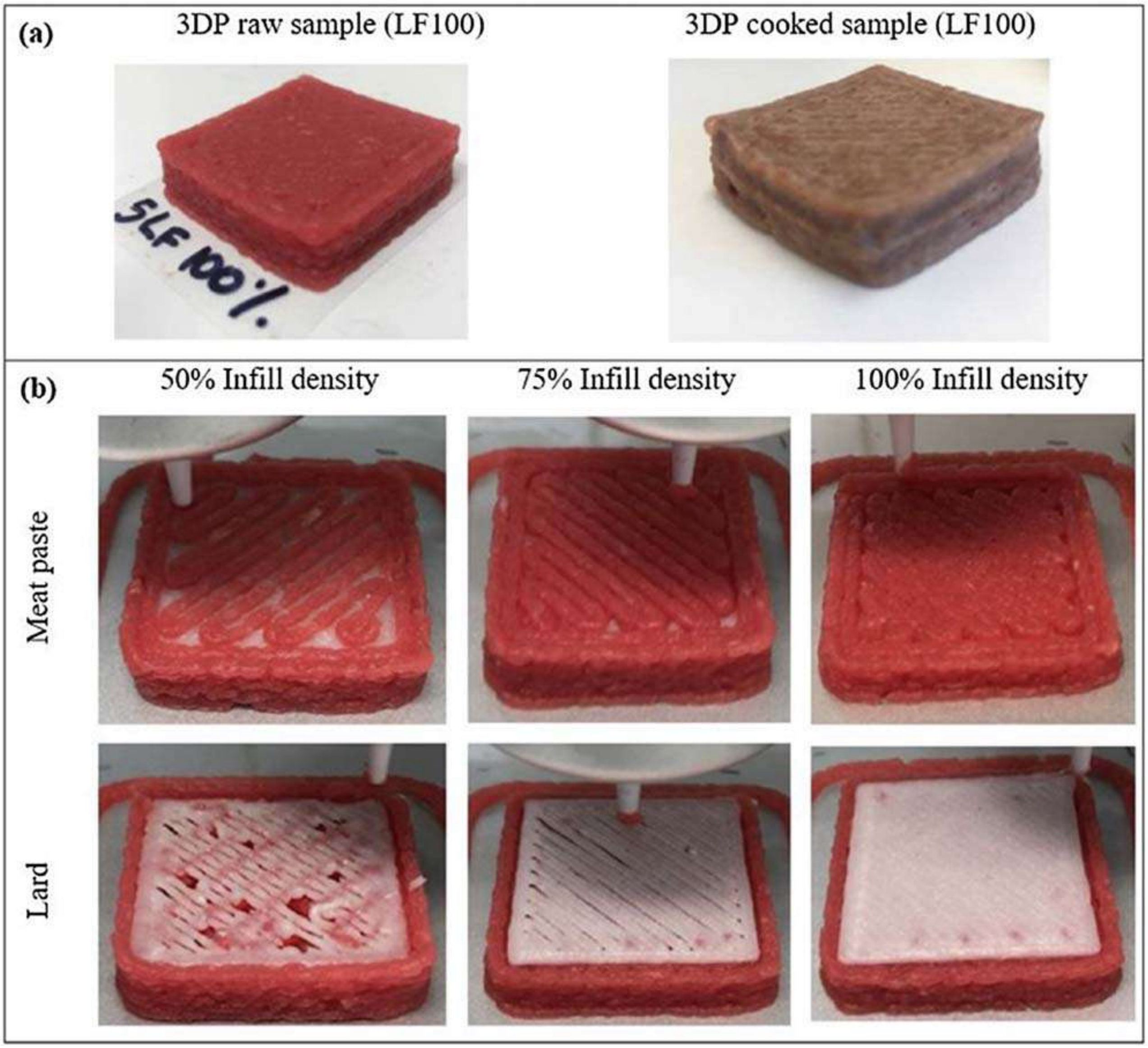

FIGURE 20.8 3D-printed composite multilayer meat models: (A) Raw and cooked samples (LF100: 1 layer of lard, 100% infill density); (B) filament stream at different infill densities (50%, 75%, and 100%) for meat paste (2 mm nozzle diameter) and lard (1 mm nozzle diameter) [26]. *Reprinted from [26], Copyright (2019), with permission from Elsevier.*

20.4 Bio

Medicine and its related fields are one of the sectors that have benefited the most in recent years with the development of 3D printing, given the large number of research in the area (Fig. 20.2). These technologies allow the development of complex and customizable systems, both in the geometric aspect and in the field of materials, which fit perfectly with the enigmatic science of living beings. Quick and adaptable measures can be the way to future solutions when it comes to saving lives or making them happier and more inclusive.

It is notable that the production of systems and materials for tissue regeneration, such as scaffolds, remains one of the main research topics in the field of biological/medical 3D printing. Many polymers can be used to build these structures, such as gels based on hyaluronic acid [31], polysaccharides (pullulan) [32], poly(ε-caprolactone) (PCL) [33–35], poly(L-lactic acid-co-ε-caprolactone) (PLCL) [36], and poly(lactic acid) (PLA) foams [37], among others.

3D printing moves toward a futuristic scenario in the research for the construction of functional organs. However, the dissemination of research is still in an embryonic, although promising, stage. Recently, researchers at Tel Aviv University, Israel, accomplished one of the great goals in medicine and engineering, when they printed the world's first vascularized heart, obtained from the patient's own cells. The cells were mixed with an extracellular matrix based on collagen and hydroproteins, giving rise to a printable hydrogel [38,39].

Another medical revolution was the concept of a functional lung, printed by scientists at Rice University. It was built using the Stereolithography technique and a hydrogel as material [40,41]. Despite being ambitious, the mentioned studies create hopes for those suffering from several diseases that compromise the functioning of vital organs, often leading to their total failure. The evolution of these research studies would be a real revolution in the process of transplants and in prolonging the lives of many people.

For now, an interesting movement was observed when the research was related to 3D printing of prostheses. There were a considerable number of initiatives to develop low-cost systems, clearly demonstrating a process of "popularization of popularization," that is, the democratization of technologies in favor of accessibility and social development. Studies show projects for the construction of stents [42], prosthetic feet [43,44], hands [45], and arms, being the latter focused on amputee victims of war [46,47] and children [48,49]. The studies are basically focused on the use of extrusion-based AM with thermoplastics such as: PLA, Acrylonitrile Butadiene Styrene (ABS), poly(ethylene terephthalate glycol) (PETG), thermoplastic polyurethane (TPU), and Elastomeric (TPE), among others.

Ferreira and his coauthors [45] developed a low-cost customized hand prosthesis in PLA by AM, considering the principles of the project e-Nable [50]. The goal was improving the aesthetic aspect, thumb movement, fingers dimensions and functionality close to reality, better adaptation, and adherence to objects due to fingertips and hand palm on flexible material − TPE (Filaflex); and all components are hidden inside the hand (Fig. 20.9).

The authors of this chapter are working in the development of novel vaginal meshes, less strong and stiff, that match the physiologic biomechanics of vaginal support. The technology of melt electrospinning equipment, with AM capability, to produce complex 3D structures from micron scale fibers, in direct 3D printing mode of medical grade thermoplastics has been developed and tested. The goal is to produce new concepts of bioabsorbable/biodegradable meshes/scaffolds with new geometries, for pelvic floor prolapse repair.

To conclude this topic, at the time of writing (April 2020) the world is dealing with one of its worst health crises, the COVID-19 (coronavirus) pandemic. It is unimaginable how something microscopic could have challenged all of humanity's technology and science, and simultaneously the way of thinking about life on earth.

In these difficult times, 3D printing showed how it can be a real "survival kit." Many models of face masks and shields are being built, using, for example, SLS with polyamide [51] (Fig. 20.10) or extrusion-based 3D printing with PLA [52]. Respirator parts were also manufactured by companies like 3D Systems, using SLS with medical grade Nylon [53]. And perhaps the most emblematic component of this battle was the supports for facial shields, in many of the cases obtained in PLA and PETG. Driven by companies like Prusa Research [54], several parts (Fig. 20.11) have been produced by the maker community and other factories such as Nagami Design (of printed furniture) [55], Airbus [56], Sandvik [57], and Materialise [58], among others.

FIGURE 20.9 Low-cost 3D-printed hand prosthesis. (Source: *courtesy of Professor Jorge Lino).*

FIGURE 20.10 Protective mask printed and its components: (A) reusable 3D-printed face mask, (B) filter membrane support, (C) polypropylene (PP) non-woven melt-blown particle filter, and (D) 3D image of the prototype [51]. *Reprinted from [51], Copyright (2020), with permission from Elsevier.*

20.5 Composites

In fact, composites have dominated the 3D printing research field. It does make a lot of sense, since there is a need for scientific production and the study of processes alone (using traditional raw materials) is already somewhat stabilized. Therefore, the formulation of new materials "unbalances the balance" and a new cycle on construction parameters and technological aspects begins.

The evaluation of materials with glass and carbon fiber reinforcements and wood continues to be studied and has already been discussed in previous chapters of this book. However, the bibliometric analysis revealed there is a trend in growth in research with conductive polymeric materials and their potential, and therefore this topic will pay attention to these elements.

One of the rising applications for conductive polymeric materials is their use to produce systems for electromagnetic shielding. Schmitz et al. [59], Ecco et al. [60], and Yin et al. [61] exploit this property through extrusion-based 3D printing using ABS with carbon nanotubes (CNTs), carbon black (CB), and graphene, in addition to PLA with carbon fibers. There are also studies on the use of photopolymers with magnetic nanoparticles (MNPs) charges for use in magnetic particle imaging (MPI) phantoms [62], in the manufacture of magnets, based on resins for SLA with black iron oxide (Fe_3O_4) [63], or even in the production of magnetic elastomers (TPU) [64].

FIGURE 20.11 Printed support for face shield (A), complete face shield (B), and respirators parts (C). (Source: *the Authors*).

Another field in evidence is the production of piezoelectric components. The structure of a microphone, for example, was built by Tiller et al. [65] using digital light processing (DLP) technology with composite resins based on poly(ethylene glycol) diacrylate (PEGDA) and barium titanium nanopowders for piezoelectric parts, and with multiwalled CNTs for conductive elements. In this context, other products such as piezoelectric nanogenerators [66] and multiaxial [67] or bidirectional elastic [68] piezoresistive sensors are also presented. In these latest studies, the conductive composites used a polymeric matrix of poly(vinylidene fluoride-co-trifluoroethylene) and PU, respectively.

Polymers with electrical conduction properties are used in the manufacture of capacitors [69] and supercapacitors [70], 3D electronic circuits [71], Wi-Fi systems [72], pressure sensors for biological applications [73], scaffolds for recovery of peripheral nerves [74], etc. These materials, therefore, take AM to a new stage in search of self-sustainability, since it starts to produce components in the context of both mechanics and electronics, being beneficial in a scenario in which Mechatronics and Automation Engineering have been leading new project guidelines for the most diverse sectors of both economy and society.

20.6 Smart polymers

We chose this as the last topic because it will address the future of AM and the materials that govern it: 4D printing. For many it is a new revolution in the means of production, and indeed it is, since it implies a series of changes such as the intellectual recycling of designers, in terms of design and selection of materials (stimuli), and social, in which time will not only be seen on clocks but on everything that is palpable to us.

4D technology does not necessarily involve the development of new equipment, with a new layer forming agent, but rather the union of traditional 3D printing techniques with design methods and smart materials, among which are polymers with the capacity of transforming over time as a response to external stimuli.

Smart polymers are materials capable of undergoing reversible, large, physical, and chemical changes in their properties due to variations in the environment, whether caused by thermal, pH, electrical, magnetic, or luminosity stimuli, among others [75]. Just as it happened with 3D printing, most studies in 4D printing, at this time, are related to the characterization of raw materials, analysis of process parameters, design of parts, and the strategic distribution of materials in its structure. Therefore, it is believed that this scenario will extend over the next few years.

However, there are also studies aimed at potential applications of the 4D technique. Animated foods can be the future on the tables of our homes or restaurants; at least that is what the 4D printing of potato-based composites shows. They were evaluated for their ability to change color over time, depending on the variation of pH [76,77].

Materials with the ability to generate large deformations through a stimulus can be potential for use in civil construction. This is what Wagner, Chen, and Shea [78] propose. The authors present a meta-material, based on the VeroWhite Plus resin, with shape memory, capable of producing parts with complex geometries and changes in area of up to 200% when in contact with hot water. Nonetheless, the study that most approximates the use of 4D printing for building houses is the one carried out by Henriques [79]. The researcher shows origami-based models for emergency shelters, printed in small scale, using an SMP (shape memory polymer) thermoplastic. The project shows structures capable of being folded, after immersion in hot water, in order to favor the transport and assembly of the system at the place of use. When exposed to the stimulus again, the piece regains its initial shape (Fig. 20.12).

4D printing can also be used in the planning of nature-inspired smart solar concentrators [80], or in the projects of plant leaf—mimetic smart wind turbine blades [81] — in both cases using PLA. Such technique is also seen in the production of smart fabrics using PLA as printing material, deposited on Nylon cloths [82], and in making jewelry and accessories for shoes, based on PCL [83].

Areas such as Medicine have also benefited greatly from the advances in 4D AM, especially in the construction of scaffolds (PLA/Fe_3O_4) [84], piezoelectric systems (Polyamide 11 with barium titanate) [85], drug delivery devices (using poly(vinyl alcohol), PVA) [86,87], and orthoses (printed Nylon parts, postprocessed with fluid iron) [88]. Our goal was not reporting all innovations related to AM but gather here some examples of what this market may provide us in the future. These are ideas that at first seem very enthusiastic, but this is the human being on his search for self-improvement. Dimensions are not the limit.

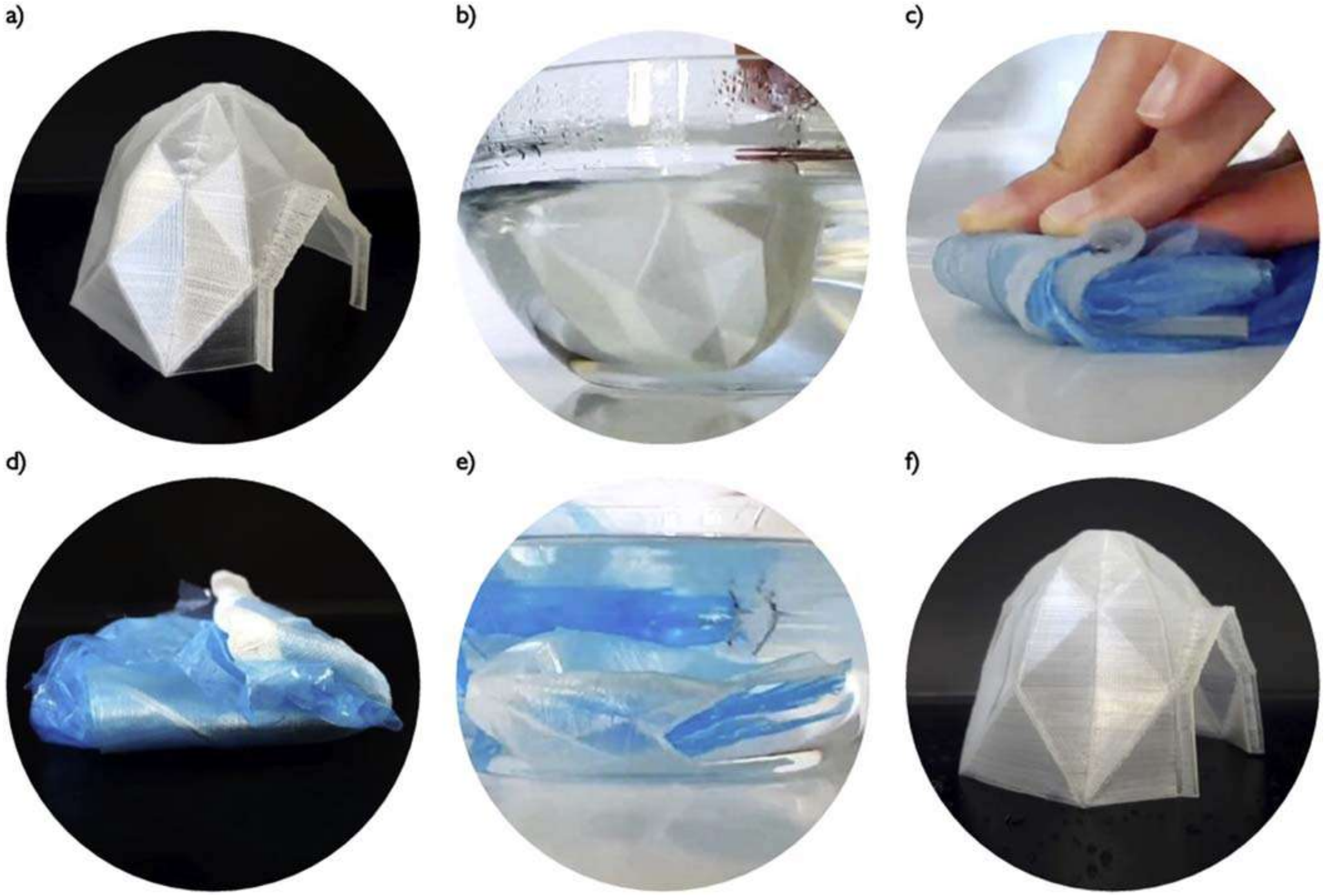

FIGURE 20.12 Printed shelter (A), hot water immersion (B), shape alteration (folding) (C) and (D), second water immersion (E), and return to the original shape (F) [79]. *Reprinted from [79], Copyright (2019), with permission from Professor Jorge Lino (Supervisor).*

20.7 Final considerations

Through a simple analysis of the literature it was possible to draw a panorama of what is being studied in 3D/4D printing and it is easy to see how it is getting closer to our daily lives, or rather, perhaps the vision is how everyday life drives research in AM. In this scenario, polymeric materials and their different formulations guide new research. However, what is perceived is that the tireless search for the aforementioned self-overcoming will make the human being enter a new cycle of production of technologies. It will be more focused on the development of machines and additive techniques that allow the manufacture of parts with dimensions varying from the minimum possible scale to colossal ones, with increasing volumes and printing speeds.

Although it was not a specific search term, the technology with the greatest approach in the area's literature is extrusion-based 3D printing, which clearly demonstrates that the ideal of popularization and democratization process, proposed by the RepRap and Fab@home movements, was achieved on merits. When 3D printing reached the world of enthusiasts, it broke the barriers of sameness and made academic research more daring and attractive.

References

[1] M.M. Reda Taha, M. Genedy, Y. Ohama, Polymer concrete, in: S. Mindess (Ed.), Developments in the Formulation and Reinforcement of Concrete, second ed., Elsevier, 2019, pp. 391–408, https://doi.org/10.1016/B978-0-08-102616-8.00017-4.

[2] K.-S. Yeon, K.K. Kim, J. Yeon, H.J. Lee, Fresh properties of EVA-modified cementitious mixtures for use in additive construction by extrusion, Materials 12 (2019) 2292, https://doi.org/10.3390/ma12142292.

[3] K.-S. Yeon, K.K. Kim, J. Yeon, H.J. Lee, Compressive and flexural strengths of EVA-modified mortars for 3D additive construction, Materials 12 (2019) 2600, https://doi.org/10.3390/ma12162600.

[4] Y. Kim, Y. Lee, Feasibility study of SBR-modified cementitious mixtures for use as 3D additive construction materials, Polymers 11 (2019) 1321, https://doi.org/10.3390/polym11081321.

[5] Y. Kim, Y. Lee, Strength development characteristics of SBR-modified cementitious mixtures for 3-demensional concrete printing, Sustainability 11 (2019) 4164, https://doi.org/10.3390/su11154164.

[6] E. Hosseini, M. Zakertabrizi, A.H. Korayem, G. Xu, A novel method to enhance the interlayer bonding of 3D printing concrete: an experimental and computational investigation, Cement Concr. Compos. 99 (2019) 112–119, https://doi.org/10.1016/j.cemconcomp.2019.03.008.

[7] B. Furet, P. Poullain, S. Garnier, 3D printing for construction based on a complex wall of polymer-foam and concrete, Addit. Manuf. 28 (2019) 58–64, https://doi.org/10.1016/j.addma.2019.04.002.

[8] Emerging Objects, Star Lounge, 2015, https://www.emergingobjects.com/project/star-lounge/ (Accessed 22 April 2020).

[9] R. Rael, V. San Frantello, Printing Architecture: Innovative Recipes for 3D Printing, first ed., Princeton Architectural Press, New York, NY, 2018.

[10] L. Camargo, N.R. Rolo, J.L. Alves, Design Generativo e Impressão 3D Aplicados ao Desenvolvimento de Mobiliário, Rev. Robótica. 115 (2019) 28–31.

[11] L. Camargo, R. de L. Rolo, J.L. Alves, Diseño Generativo e Impresión 3D Aplicado al Desarrollo de Muebles, in: Memórias Do XIV Congr. Iberoam. Ing. Mecánica, Cartagena, 2019.

[12] V.H.P. Carneiro, Development of Lightweight Auxetic Composites for Noise Reduction and Vibration Damping, Universidade do Minho, 2019.

[13] V.H. Carneiro, H. Puga, J. Meireles, Positive, Zero and negative poison's ratio non-stochastic metallic cellular solids: dependence between static and dynamic mechanical properties, Compos. Struct. 226 (2019) 111239, https://doi.org/10.1016/j.compstruct.2019.111239.

[14] X. Liu, F. Xie, X. Li, S. Zhou, L. Chen, Food polymers functionality and applications, Int. J. Polym. Sci. 2015 (2015), https://doi.org/10.1155/2015/813628, 1–1.

[15] J. Milani, G. Maleki, Hydrocolloids in food industry, in: B. Valdez (Ed.), Food Industrial Processes – Methods and Equipment, InTech, 2012, pp. 17–37, https://doi.org/10.5772/32358.

[16] H. Zhang, F. Zhang, R. Yuan, Applications of natural polymer-based hydrogels in the food industry, in: Y. Chen (Ed.), Hydrogels Based on Natural Polymers, Elsevier, 2020, pp. 357–410, https://doi.org/10.1016/B978-0-12-816421-1.00015-X.

[17] L. Dai, T. Cheng, C. Duan, W. Zhao, W. Zhang, X. Zou, J. Aspler, Y. Ni, 3D printing using plant-derived cellulose and its derivatives: a review, Carbohydr. Polym. 203 (2019) 71–86, https://doi.org/10.1016/j.carbpol.2018.09.027.

[18] Z. Liu, B. Bhandari, S. Prakash, S. Mantihal, M. Zhang, Linking rheology and printability of a multicomponent gel system of carrageenan-xanthan-starch in extrusion based additive manufacturing, Food Hydrocoll. 87 (2019) 413–424, https://doi.org/10.1016/j.foodhyd.2018.08.026.

[19] J. Chen, T. Mu, D. Goffin, C. Blecker, G. Richard, A. Richel, E. Haubruge, Application of soy protein isolate and hydrocolloids based mixtures as promising food material in 3D food printing, J. Food Eng. 261 (2019) 76–86, https://doi.org/10.1016/j.jfoodeng.2019.03.016.

[20] L. Liu, Y. Meng, X. Dai, K. Chen, Y. Zhu, 3D printing complex egg white protein objects: properties and optimization, Food Bioprocess Technol. 12 (2019) 267–279, https://doi.org/10.1007/s11947-018-2209-z.

[21] Y. Liu, Y. Yu, C. Liu, J.M. Regenstein, X. Liu, P. Zhou, Rheological and mechanical behavior of milk protein composite gel for extrusion-based 3D food printing, LWT 102 (2019) 338–346, https://doi.org/10.1016/j.lwt.2018.12.053.

[22] F. Yang, M. Zhang, B. Bhandari, Y. Liu, Investigation on lemon juice gel as food material for 3D printing and optimization of printing parameters, LWT 87 (2018) 67–76, https://doi.org/10.1016/j.lwt.2017.08.054.

[23] H.W. Kim, I.J. Lee, S.M. Park, J.H. Lee, M.-H. Nguyen, H.J. Park, Effect of hydrocolloid addition on dimensional stability in post-processing of 3D printable cookie dough, LWT 101 (2019) 69–75, https://doi.org/10.1016/j.lwt.2018.11.019.

[24] L. Wang, M. Zhang, B. Bhandari, C. Yang, Investigation on fish surimi gel as promising food material for 3D printing, J. Food Eng. 220 (2018) 101−108, https://doi.org/10.1016/j.jfoodeng.2017.02.029.

[25] H.W. Kim, J.H. Lee, S.M. Park, M.H. Lee, I.W. Lee, H.S. Doh, H.J. Park, Effect of hydrocolloids on rheological properties and printability of vegetable inks for 3D food printing, J. Food Sci. 83 (2018) 2923−2932, https://doi.org/10.1111/1750-3841.14391.

[26] A. Dick, B. Bhandari, S. Prakash, Post-processing feasibility of composite-layer 3D printed beef, Meat Sci. 153 (2019) 9−18, https://doi.org/10.1016/j.meatsci.2019.02.024.

[27] C. Le Tohic, J.J. O'Sullivan, K.P. Drapala, V. Chartrin, T. Chan, A.P. Morrison, J.P. Kerry, A.L. Kelly, Effect of 3D printing on the structure and textural properties of processed cheese, J. Food Eng. 220 (2018) 56−64, https://doi.org/10.1016/j.jfoodeng.2017.02.003.

[28] J.K. Adewole, K.B. Muritala, Some applications of natural polymeric materials in oilfield operations: a review, J. Pet. Explor. Prod. Technol. 9 (2019) 2297−2307, https://doi.org/10.1007/s13202-019-0626-9.

[29] F.Y. de Boer, A. Imhof, K.P. Velikov, Encapsulation of colorants by natural polymers for food applications, Color. Technol. 135 (2019) 183−194, https://doi.org/10.1111/cote.12393.

[30] R. Bailey, Biological Polymers: Proteins, Carbohydrates, Lipids, 2019. https://www.thoughtco.com/biological-polymers-373562 (Accessed 10 April 2020).

[31] L. Wei, S. Wu, M. Kuss, X. Jiang, R. Sun, P. Reid, X. Qin, B. Duan, 3D printing of silk fibroin-based hybrid scaffold treated with platelet rich plasma for bone tissue engineering, Bioact. Mater. 4 (2019) 256−260, https://doi.org/10.1016/j.bioactmat.2019.09.001.

[32] G. Della Giustina, A. Gandin, L. Brigo, T. Panciera, S. Giulitti, P. Sgarbossa, D. D'Alessandro, L. Trombi, S. Danti, G. Brusatin, Polysaccharide hydrogels for multiscale 3D printing of pullulan scaffolds, Mater. Des. 165 (2019) 107566, https://doi.org/10.1016/j.matdes.2018.107566.

[33] H. Liu, A. Ahlinder, M.A. Yassin, A. Finne-Wistrand, T.C. Gasser, Computational and experimental characterization of 3D-printed PCL structures toward the design of soft biological tissue scaffolds, Mater. Des. 188 (2020) 108488, https://doi.org/10.1016/j.matdes.2020.108488.

[34] D. Sooriyaarachchi, J. Wu, A. Feng, M. Islam, G.Z. Tan, Hybrid fabrication of biomimetic meniscus scaffold by 3D printing and parallel electrospinning, Procedia Manuf. 34 (2019) 528−534, https://doi.org/10.1016/j.promfg.2019.06.216.

[35] W. Zhang, I. Ullah, L. Shi, Y. Zhang, H. Ou, J. Zhou, M.W. Ullah, X. Zhang, W. Li, Fabrication and characterization of porous polycaprolactone scaffold via extrusion-based cryogenic 3D printing for tissue engineering, Mater. Des. 180 (2019) 107946, https://doi.org/10.1016/j.matdes.2019.107946.

[36] W. Liu, Z. Feng, W. Ou-Yang, X. Pan, X. Wang, P. Huang, C. Zhang, D. Kong, W. Wang, 3D printing of implantable elastic PLCL copolymer scaffolds, Soft Matter 16 (2020) 2141−2148, https://doi.org/10.1039/C9SM02396H.

[37] W.J. Choi, K.S. Hwang, H.J. Kwon, C. Lee, C.H. Kim, T.H. Kim, S.W. Heo, J.-H. Kim, J.-Y. Lee, Rapid development of dual porous poly(lactic acid) foam using fused deposition modeling (FDM) 3D printing for medical scaffold application, Mater. Sci. Eng. C 110 (2020) 110693, https://doi.org/10.1016/j.msec.2020.110693.

[38] Tel Aviv University, TAU Scientists Print First Ever 3D Heart Using Patient's Own Cells, 2019. https://english.tau.ac.il/news/printed_heart (Accessed 12 April 2020).

[39] N. Noor, A. Shapira, R. Edri, I. Gal, L. Wertheim, T. Dvir, 3D printing of personalized thick and perfusable cardiac patches and hearts, Adv. Sci. 6 (2019) 1900344, https://doi.org/10.1002/advs.201900344.

[40] L. Gaget, Discover the First 3D Printed Lung, 2019. https://www.sculpteo.com/blog/2019/05/22/discover-the-first-3d-printed-lung/ (Accessed 12 April 2020).

[41] B. Grigoryan, S.J. Paulsen, D.C. Corbett, D.W. Sazer, C.L. Fortin, A.J. Zaita, P.T. Greenfield, N.J. Calafat, J.P. Gounley, A.H. Ta, F. Johansson, A. Randles, J.E. Rosenkrantz, J.D. Louis-Rosenberg, P.A. Galie, K.R. Stevens, J.S. Miller, Multivascular networks and functional intravascular topologies within biocompatible hydrogels, Science 364 (2019) 458−464, https://doi.org/10.1126/science.aav9750.

[42] B.A. Malafaya, M.C. Marques, I.A. Ferreira, M.M.F. Machado, G.A.R. Caldas, J. Belinha, F.J.L. Alves, R.M.N. Jorge, Development of PLA-based stent uusing fused deposition modeling, in: 3rd Doctoral Congress in Engineering FEUP, 2019.

[43] R.K. Chaithanya, C. Sanjay, Design of 3D printed low cost multi axis prosthetic foot, Int. J. Des. Manuf. Technol. 10 (2019) 12−18, https://doi.org/10.34218/IJDMT.10.1.2019.002.

[44] H. Kamel, O. Harraz, K. Azab, T. Attia, Developing an optimized low-cost transtibial energy storage and release prosthetic foot using three-dimensional printing, J. Eng. Sci. Med. Diagnostics Ther. 3 (2020), https://doi.org/10.1115/1.4046319.

[45] D. Ferreira, T. Duarte, J.L. Alves, I. Ferreira, Development of low-cost customised hand prostheses by additive manufacturing, Plast. Rubber Compos. 47 (2018) 25−34, https://doi.org/10.1080/14658011.2017.1413793.

[46] F. Alkhatib, E. Mahdi, J.-J. Cabibihan, Design and analysis of flexible joints for a robust 3D printed prosthetic hand, in: 2019 IEEE 16th International Conference on Rehabilitation Robotics, IEEE, 2019, pp. 784−789, https://doi.org/10.1109/ICORR.2019.8779372.

[47] R. Neethan, S. Nidershan, V. Mugilgeethan, T. Tharsika, A. Anburuvel, A study of three-dimensional (3-D) printed prosthetic upper limb models in local context, Mater. Today Proc. 23 (2020) 8−11, https://doi.org/10.1016/j.matpr.2019.05.348.

[48] S.M. Kellam, G.J. Boleneus, J. Stewart, C. Donald, P.E. Richter, B.M. Michaelis, R.E. Gerlick, An undergraduate engineering service learning project involving 3D-printed prosthetic hands for children, in: 2019 ASEE Annual Conference & Expo, American Society for Engineering Education, Tampa, FL, 2019. https://www.asee.org/public/conferences/140/papers/26715/view.

[49] J.M. Zuniga, J.L. Peck, R. Srivastava, J.E. Pierce, D.R. Dudley, N.A. Than, N. Stergiou, Functional changes through the usage of 3D-printed transitional prostheses in children, Disabil. Rehabil. Assist. Technol. 14 (2019) 68−74, https://doi.org/10.1080/17483107.2017.1398279.

[50] E-NABLE, Enabling the Future, 2020. http://enablingthefuture.org/ (Accessed 14 May 2020).

[51] G.R.J. Swennen, L. Pottel, P.E. Haers, Custom-made 3D-printed face masks in case of pandemic crisis situations with a lack of commercially available FFP2/3 masks, Int. J. Oral Maxillofac. Surg. 49 (2020), https://doi.org/10.1016/j.ijom.2020.03.015.

[52] D. Provenzano, Y.J. Rao, K. Mitic, S.N. Obaid, D. Pierce, J. Huckenpahler, J. Berger, S. Goyal, M.H. Loew, Rapid Prototyping of Reusable 3D-Printed N95 Equivalent Respirators, 2020, https://doi.org/10.20944/preprints202003.0444.v1. George Washington University, Prepr. 2020.

[53] 3D Systems, COVID-19 Call to Action, 2020. https://www.3dsystems.com/covid-19-response (Accessed 13 April 2020).

[54] Prusa Research, 3D Printed Face Shields for Medics and Professionals, 2020. https://www.prusa3d.com/covid19/ (Accessed 13 April 2020).

[55] I. Block, Nagami Design 3D-Prints Face Shields to Protect Medical Staff from Coronavirus, 2020. https://www.dezeen.com/2020/03/27/3d-printed-face-shields-coronavirus-covid-19-masks-nagami-design/ (Accessed 13 April 2020).

[56] M. Paul, Airbus to Produce 3D-Printed Hospital Visors in Fight against Covid-19, 2020. https://www.traveldailymedia.com/airbus-to-produce-3d-printed-hospital-visors-in-fight-against-covid-19/ (Accessed 13 April 2020).

[57] Sandvik, Sandvik Provides Support to Protect Healthcare Workers in the Battle against Covid-19 by Using 3D-Printing, 2020. https://www.additive.sandvik/en/news-trends/archive/2020/04/sandvik-provides-support-to-protect-healthcare-workers-in-the-battle-against-covid-19-by-using-3d-printing/ (Accessed 13 April 2020).

[58] Materialise, Materialise Develops 3D Printed Oxygen PEEP Mask to Address Shortage of Ventilators, 2020. https://www.materialise.com/en/press-releases/materialise-develops-3d-printed-oxygen-peep-mask-to-address-shortage-of-ventilators (Accessed 14 May 2020).

[59] D.P. Schmitz, L.G. Ecco, S. Dul, E.C.L. Pereira, B.G. Soares, G.M.O. Barra, A. Pegoretti, Electromagnetic interference shielding effectiveness of ABS carbon-based composites manufactured via fused deposition modelling, Mater. Today Commun. 15 (2018) 70−80, https://doi.org/10.1016/j.mtcomm.2018.02.034.

[60] L. Ecco, S. Dul, D. Schmitz, G. Barra, B. Soares, L. Fambri, A. Pegoretti, Rapid prototyping of efficient electromagnetic interference shielding polymer composites via fused deposition modeling, Appl. Sci. 9 (2018) 37, https://doi.org/10.3390/app9010037.

[61] L. Yin, X. Tian, Z. Shang, X. Wang, Z. Hou, Characterizations of continuous carbon fiber-reinforced composites for electromagnetic interference shielding fabricated by 3D printing, Appl. Phys. A 125 (2019) 266, https://doi.org/10.1007/s00339-019-2566-0.

[62] N. Löwa, J.-M. Fabert, D. Gutkelch, H. Paysen, O. Kosch, F. Wiekhorst, 3D-printing of novel magnetic composites based on magnetic nanoparticles and photopolymers, J. Magn. Magn. Mater. 469 (2019) 456−460, https://doi.org/10.1016/j.jmmm.2018.08.073.

[63] S. Safaee, R. Chen, Investigation of a magnetic field-assisted digital-light-processing Stereolithography for functionally graded materials, Procedia Manuf. 34 (2019) 731−737, https://doi.org/10.1016/j.promfg.2019.06.229.

[64] A.H. Morgenstern, T.M. Calascione, N.A. Fischer, T.J. Lee, J.E. Wentz, B.B. Nelson-Cheeseman, Thermoplastic magnetic elastomer for fused filament fabrication, AIMS Mater. Sci. 6 (2019) 363−376, https://doi.org/10.3934/matersci.2019.3.363.

[65] B. Tiller, A. Reid, B. Zhu, J. Guerreiro, R. Domingo-Roca, J. Curt Jackson, J.F.C. Windmill, Piezoelectric microphone via a digital light processing 3D printing process, Mater. Des. 165 (2019) 107593, https://doi.org/10.1016/j.matdes.2019.107593.

[66] X. Zhou, K. Parida, O. Halevi, Y. Liu, J. Xiong, S. Magdassi, P.S. Lee, All 3D-printed stretchable piezoelectric nanogenerator with non-protruding kirigami structure, Nano Energy 72 (2020) 104676, https://doi.org/10.1016/j.nanoen.2020.104676.

[67] S. Kwon, S. Kim, I. Kim, Y.K. Hong, S. Na, Direct 3D printing of graphene nanoplatelet/silver nanoparticle-based nanocomposites for multiaxial piezoresistive sensor applications, Adv. Mater. Technol. 4 (2019) 1800500, https://doi.org/10.1002/admt.201800500.

[68] J. Christ, N. Aliheidari, P. Pötschke, A. Ameli, Bidirectional and stretchable piezoresistive sensors enabled by multimaterial 3D printing of carbon nanotube/thermoplastic polyurethane nanocomposites, Polymers 11 (2018) 11, https://doi.org/10.3390/polym11010011.

[69] N.I. Jaksic, P.D. Desai, Characterization of 3D-printed capacitors created by fused filament fabrication using electrically-conductive filament, Procedia Manuf. 38 (2019) 33−41, https://doi.org/10.1016/j.promfg.2020.01.005.

[70] R. Gusmão, M.P. Browne, Z. Sofer, M. Pumera, The capacitance and electron transfer of 3D-printed graphene electrodes are dramatically influenced by the type of solvent used for pre-treatment, Electrochem. Commun. 102 (2019) 83−88, https://doi.org/10.1016/j.elecom.2019.04.004.

[71] S.W. Kwok, K.H.H. Goh, Z.D. Tan, S.T.M. Tan, W.W. Tjiu, J.Y. Soh, Z.J.G. Ng, Y.Z. Chan, H.K. Hui, K.E.J. Goh, Electrically conductive filament for 3D-printed circuits and sensors, Appl. Mater. Today. 9 (2017) 167−175, https://doi.org/10.1016/j.apmt.2017.07.001.

[72] V. Iyer, J. Chan, S. Gollakota, 3D printing wireless connected objects, ACM Trans. Graph. 36 (2017) 242:1−242:13, https://doi.org/10.1145/3130800.3130822.

[73] J. Park, J.-K. Kim, D.-S. Kim, A. Shanmugasundaram, S.A. Park, S. Kang, S.-H. Kim, M.H. Jeong, D.-W. Lee, Wireless pressure sensor integrated with a 3D printed polymer stent for smart health monitoring, Sensor. Actuator. B Chem. 280 (2019) 201−209, https://doi.org/10.1016/j.snb.2018.10.006.

[74] S. Vijayavenkataraman, S. Thaharah, S. Zhang, W.F. Lu, J.Y.H. Fuh, Electrohydrodynamic jet 3D-printed PCL/PAA conductive scaffolds with tunable biodegradability as nerve guide conduits (NGCs) for peripheral nerve injury repair, Mater. Des. 162 (2019) 171−184, https://doi.org/10.1016/j.matdes.2018.11.044.

[75] M.R. Aguilar, J.S. Román, Introduction to smart polymers and their applications, in: second ed., in: M.R. Aguilar, J.S. Román (Eds.), Smart Polymers and Their Applications, vol. 2019, Woodhead Publishing, 2019, pp. 1−11.

[76] C. He, M. Zhang, C. Guo, 4D printing of mashed potato/purple sweet potato puree with spontaneous color change, Innovat. Food Sci. Emerg. Technol. 59 (2020) 102250, https://doi.org/10.1016/j.ifset.2019.102250.

[77] A.F. Ghazal, M. Zhang, Z. Liu, Spontaneous color change of 3D printed healthy food product over time after printing as a novel application for 4D food printing, Food Bioprocess Technol. 12 (2019) 1627−1645, https://doi.org/10.1007/s11947-019-02327-6.

[78] M. Wagner, T. Chen, K. Shea, Large shape transforming 4D auxetic structures, 3D print, Addit. Manuf. 4 (2017) 133−141, https://doi.org/10.1089/3dp.2017.0027.

[79] L.A.C. Henriques, 4D Structures for Rapid Construction of a Shelter in Crisis Situations, Universidade do Porto, 2019.

[80] F. Momeni, J. Ni, Nature-inspired smart solar concentrators by 4D printing, Renew. Energy 122 (2018) 35−44, https://doi.org/10.1016/j.renene.2018.01.062.

[81] F. Momeni, S. Sabzpoushan, R. Valizadeh, M.R. Morad, X. Liu, J. Ni, Plant leaf-mimetic smart wind turbine blades by 4D printing, Renew. Energy 137 (2019) 329−351, https://doi.org/10.1016/j.renene.2018.05.095.

[82] S.K. Leist, D. Gao, R. Chiou, J. Zhou, Investigating the shape memory properties of 4D printed polylactic acid (PLA) and the concept of 4D printing onto nylon fabrics for the creation of smart textiles, Virtual Phys. Prototyp. 12 (2017) 290−300, https://doi.org/10.1080/17452759.2017.1341815.

[83] M. Zarek, M. Layani, S. Eliazar, N. Mansour, I. Cooperstein, E. Shukrun, A. Szlar, D. Cohn, S. Magdassi, 4D printing shape memory polymers for dynamic jewellery and fashionwear, Virtual Phys. Prototyp. 11 (2016) 263−270, https://doi.org/10.1080/17452759.2016.1244085.

[84] W. Zhao, F. Zhang, J. Leng, Y. Liu, Personalized 4D printing of bioinspired tracheal scaffold concept based on magnetic stimulated shape memory composites, Compos. Sci. Technol. 184 (2019) 107866, https://doi.org/10.1016/j.compscitech.2019.107866.

[85] D. Grinberg, S. Siddique, M.Q. Le, R. Liang, J.F. Capsal, P.J. Cottinet, 4D printing based piezoelectric composite for medical applications, J. Polym. Sci., Part B: Polym. Phys. 52 (2019) 109−115, https://doi.org/10.1002/polb.24763.

[86] A. Melocchi, N. Inverardi, M. Uboldi, F. Baldi, A. Maroni, S. Pandini, F. Briatico-Vangosa, L. Zema, A. Gazzaniga, Retentive device for intravesical drug delivery based on water-induced shape memory response of poly(vinyl alcohol): design concept and 4D printing feasibility, Int. J. Pharm. 559 (2019) 299−311, https://doi.org/10.1016/j.ijpharm.2019.01.045.

[87] A. Melocchi, M. Uboldi, N. Inverardi, F. Briatico-Vangosa, F. Baldi, S. Pandini, G. Scalet, F. Auricchio, M. Cerea, A. Foppoli, A. Maroni, L. Zema, A. Gazzaniga, Expandable drug delivery system for gastric retention based on shape memory polymers: development via 4D printing and extrusion, Int. J. Pharm. 571 (2019) 118700, https://doi.org/10.1016/j.ijpharm.2019.118700.

[88] A.R. Ploszajski, R. Jackson, M. Ransley, M. Miodownik, 4D printing of magnetically functionalized chainmail for exoskeletal biomedical applications, MRS Adv. 4 (2019) 1361−1366, https://doi.org/10.1557/adv.2019.154.

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Methods, Properties, and Characteristics

Edited by: Joanna Izdebska-Podsiadły

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