

## Chapter 7

# Development of Soy Composites by Direct Deposition

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## Introduction

Composites are materials comprised of two or more components that differ in their chemical and physical properties, which have been combined to promote specific characteristics for particular uses. In general, composites correspond to a class of heterogeneous multiphase materials. One of the components (discontinuous) supplies the strength (structural component or reinforcement), and the other (continuous) is the medium of stress transfer (matrix). These components are not mutually dissolved, but they act in a synchronized way, and the material as a whole offers a satisfactory performance (1).

The polymeric matrices are more common in composites, although there are composites having other types of matrices, such as a metallic matrix. The most used thermosetting resins in high-performance advanced composites are the phenolics, epoxies, polyimides, bismaleimides, and cyanate ester resin systems. These resins exhibit both excellent solvent and high-temperature resistance. It has been estimated that >75% of all polymeric matrices in composites are thermoset polymers. Thermosetting polymers are resins that crosslink during the curing. Curing involves the application of heat and pressure or the addition of a catalyst.

Polymeric materials prepared from renewable natural resources have been enjoying a continuous growing interest in the past decade from the academic and applied point of view. The advantages of these polymers are their low cost, easy availability, and possible biodegradability (2). Among products from agricultural resources, natural oils may constitute raw materials useful in polymer synthesis. Annually, the United States produces ~450 thousand tons of soybean oil in excess of current commercial need. Thus, developing new materials from soybean oil for industrial application has become highly desirable. These new materials can open needed new markets for this important crop.

Epoxies have good adhesion, mechanical properties, low moisture absorption, chemical resistance, little shrinkage, and ease of processing. These excellent properties make this family of compounds one of the best matrix materials for many composites (3,4). However, epoxy resins are similar to other engineering resins in that they are either brittle, notch-sensitive, or both. For load-bearing purposes, this means that the product may be subject to catastrophic failure. A major effort over the years has focused on improving the toughness of epoxy structural systems. Qureshi *et al.* (5)

reported that the use of 25% epoxidized crambe oil as a reactive diluent in bisphenol A and cycloaliphatic epoxy compounds improved resistance to fatigue crack propagation without significant sacrifice in tensile or impact strength and Young's modulus. Massingill *et al.* (6) formulated neat epoxidized crambe oil with epoxy-amine systems to give two-phase thermosets. Fracture toughness values of the epoxy thermosets were increased ~100% by 5 and 10% epoxidized crambe oil. The glass transition temperature and mechanical properties were affected modestly. Soybean oil is a triglyceride that contains double bonds. These double bonds may also be converted into the more reactive oxirane moiety by reaction with peracids or peroxides. In the past, epoxidized soybean oil (ESO) has been used mainly as a plasticizer for polyvinyl chloride (PVC) compounds, chlorinated rubber, and polyvinyl acetate (PVA) emulsions. Epoxy-containing soybean oil used as raw material for the synthesis of new polymers suitable for liquid molding processes was reported by Wool and co-workers (7,8). The preparation of structurally strong soy-based composites is attractive from both the commercial and environmental perspectives. Reinforcement materials in soy-based composites can be glass or natural fiber.

### ***Composites Reinforced with Glass, Carbon, or Mineral Fibers***

Composites reinforced with carbon, aramid, and glass fiber dominate the aerospace, leisure, automotive, construction, and sporting industries. Glass fibers are most widely used to reinforce plastics due to their low cost (compared with aramid and carbon) and fairly good mechanical properties. These fibers have serious drawbacks as indicated in Table 7.1. The shortcomings have been highly exploited by proponents of natural fiber composites. Table 7.1 compares natural and glass fibers and clearly shows areas in which the former have distinct advantages over the latter. The carbon dioxide neutrality of natural fibers is particularly attractive. Attempts have been made to use natural fiber composites in place of glass mainly in nonstructural applications. A good number of automotive components previously

**TABLE 7.1**  
Comparison Between Natural and Glass Fibers

	Natural fibers	Glass fibers
Density	Low	Twice that of natural fibers
Cost	Low	Low, but higher than NF
Renewability	Yes	No
Recyclability	Yes	No
Energy consumption	Low	High
Distribution	Wide	Wide
CO <sub>2</sub> neutral	Yes	No
Abrasion to machines	No	Yes
Health risk when inhaled	No	Yes
Disposal	Biodegradable	Not biodegradable

made with glass fiber composites are now being manufactured using environmentally friendly composites (10,11) .

### ***Composites Reinforced with Natural Fibers***

Currently, a great deal of research material is being generated on the potential of natural fiber as a reinforcement for plastics. Natural fiber may include hairs (cotton, kapok), fiber-sheaves of dicotyled plants, or vessel-sheaves of monocotyled plants, i.e., bast (flax, hemp, jute, ramie) and hard-fiber (sisal, henequen, coir). The availability of large quantities of such fiber with well-defined mechanical properties is a general prerequisite for the successful use of these materials and the lack of these large quantities is one of the drawbacks at present. Additionally, for several more technically oriented applications, the fibers have to be specially prepared or modified regarding the following:

- homogenization of the fiber's properties;
- degrees of elementarization and degumming;
- degrees of polymerization and crystallization;
- good adhesion between fiber and matrix;
- moisture repellence; and
- flame retardant properties.

At present, the availability of plant fiber can be only partially ensured (as shown in Table 7.2).

Their hydrophilic nature is a major problem for all natural fibers if they are used as reinforcements in plastics. The moisture content of the fibers, dependent on the content of noncrystalline parts and void content of the fiber, can be as much as 10 wt% under standard conditions (12). The hydrophilic nature of natural fiber influences the overall mechanical properties as well as other physical properties of the fiber itself (13). Physical (i.e., corona discharge) and chemical modification methods (coupling agents such as silanes) are used to change the surface structure of the fibers as well as to change their surface energy.

**TABLE 7.2**

Production of Plant Fibers Compared with Production of Glass Fibers (1993)<sup>a</sup>

Fiber	Price in comparison to glass fibers (%)	Production (1000 t)
Jute	18	3600
E-glass	100	1200
Flax	130	800
Sisal	21	500
Banana	40	100

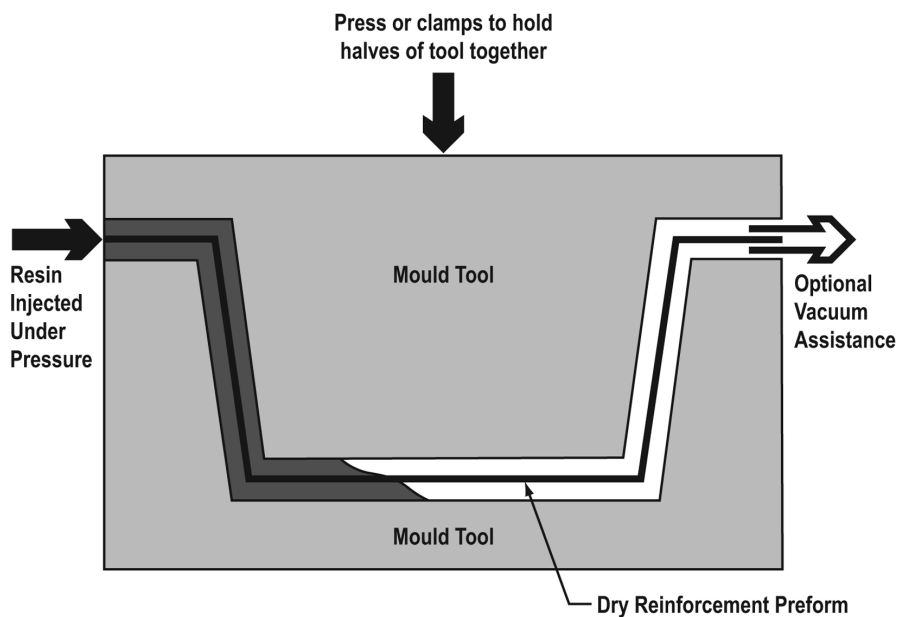
<sup>a</sup>Source: Reference 9.

## Composite Molding Methods

A wide range of different processes have been developed for the molding of composite parts ranging from very simple manual processes such as hand lay to very sophisticated highly industrialized processes such as sheet molding compounds. Each process has its own particular benefits and limitations making it suitable for particular applications. The choice of process is important to achieve the required technical performance economically. The most common molding techniques for the manufacturing of fiber reinforcement composites are resin transfer molding (RTM), vacuum-assisted resin injection (VARI), reinforced reaction injection molding (RRIM), structural reaction injection molding (S-RTM), vacuum infusion (VI), and solid free-form fabrication (SFF). These composite molding methods have been used successfully to manufacture products ranging from cosmetic parts with moderate demands for structural properties to highly load bearing parts of military and aerospace quality.

### ***Resin Transfer Molding (RTM) and Vacuum Assisted Resin Injection (VARI)***

Figure 7.1 shows a schematic of RTM. Fabrics are laid up as a dry stack of materials. These fabrics are sometimes prepressed to the mold shape, and held together by a binder. These “preforms” are then more easily laid into the mold tool. A second



**Fig. 7.1.** Schematic of resin transfer molding (RTM).

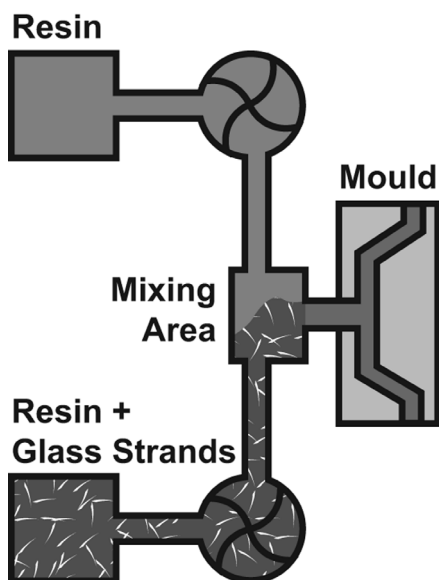
mold tool is then clamped over the first, and resin is injected into the cavity. A vacuum can also be applied to the mold cavity to assist resin in being drawn into the fabrics. This is known as Vacuum Assisted Resin Injection (VARI). Once all of the fabric is wet, the resin inlets are closed, and the laminate is allowed to cure. Both injection and cure can take place at either ambient or elevated temperature. Generally epoxy, polyester, vinyl ester and phenolic resins are used at ambient temperature, although high-temperature resins such as bismaleimides can be used at elevated process temperatures. Any kind of fiber can be used as reinforcement. Stitched materials work well in this process because the gaps allow rapid resin transport. Some specially developed fabrics can assist with resin flow. The main advantages are that high fiber volume laminates can be obtained with very low void contents and with better safety and environmental control due to the enclosure of the resin. Both sides of the component have a molded surface. Medium large, complex, and highly integrated components can be produced with low capital costs and with a good working environment. The main disadvantages are that matched tooling is expensive and has to be heavy to be able to withstand pressures. Generally RTM is limited to smaller components.

### ***Reinforced Reaction Injection Molding (RRIM) and Structural Reaction Injection Molding (SRIM)***

This is a fabrication technique involving the extremely rapid impingement mixing of two chemically reactive liquid streams, injected into a mold that results in the simultaneous polymerization, cross-linking and formation of the part. This technique is a form of reactive injection molding (RIM). [Figure 7.2](#) shows a schematic of RIM. When short fibers (1.6 mm), carbon, or glass or mineral fillers are incorporated into one of the two reactive constituents to increase the modulus and reduce the coefficient of expansion, the process is referred to as reinforced reaction injection molding (RRIM). The introduction of long-strand reinforcements, such as continuous filament mats, fabrics, complexes, or chopped strand preforms, into the mold before the injection takes place, allows parts with higher mechanical performance to be obtained. In this case, the process is known as structural reaction injection molding (SRIM). In each of these technologies, polymeric parts are produced directly from a mixture of the low-viscous reactants by its injection into a mold accompanied by fast polymerization and cross-linking reactions. The inherent advantages of RRIM and SRIM are that large parts can be produced with dimensional stability, chemical resistance, weatherability, and surface reproducibility. The main disadvantage is that it is difficult to control the volatile organic chemical (VOC) emissions from the open mold process.

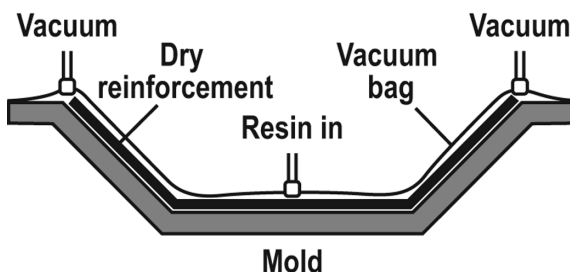
### ***Vacuum Infusion (VI)***

The vacuum infusion (VI) process has become prominent in recent years due to increasing pressure on the control of VOC emissions from the open mold process.



**Fig. 7.2.** Schematic of reaction injection molding (RIM).

Figure 7.3 shows a schematic of VI. The basic principal of VI is that reinforcing fibers are placed in a mold, which is sealed using a plastic film or vacuum bag, and resin is drawn into the mold under vacuum. It means lower injection pressure than in the RTM, with the pressure limited to 0.1 MPa. Molds for VI are fitted with a peripheral channel to enable a vacuum to be applied, and catalyzed resin is fed in at the center of the part and allowed to diffuse through the reinforcement to the edge of the mold. The design of the reinforcement and the setting up of the plastic film or vacuum bag, which normally incorporates tubes or channels to help even distribution of the resin, are absolutely critical. A major advantage of the VI process is that it can be reproduced exactly each time without the need to use skilled laminators. The mold is also fully enclosed during the molding process virtually eliminating VOC emissions. A further advantage of the use of the vacuum is

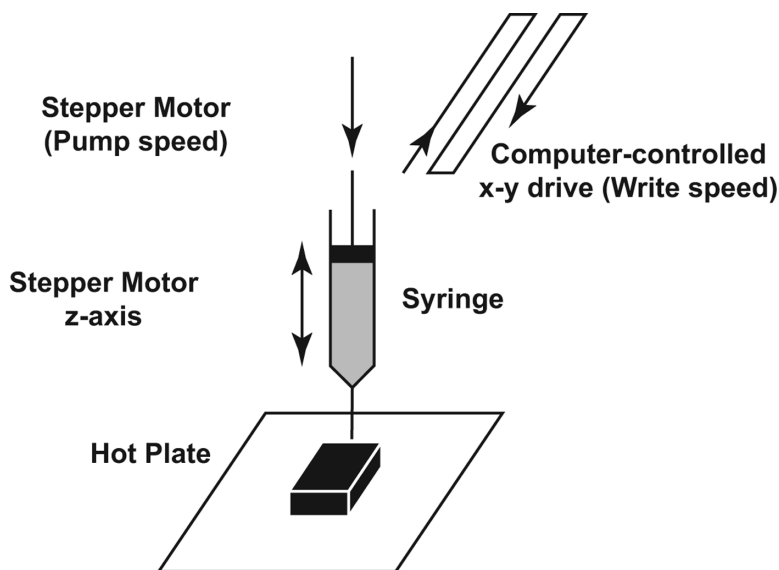


**Fig. 7.3.** Schematic of vacuum infusion (VI).

that parts are extremely well consolidated, even with a high fiber content, with very low air content giving very good structural performance. The investment costs of VI molding are low, and it is possible to produce larger parts. One disadvantage of VI is that the excellent consolidation favors thin high-fiber content parts, which may not have sufficient stiffness. Other disadvantages are that the fiber content is usually lower than RTM and only one surface of the manufactured composites is well controlled. The thickness and consequently the fiber content are not as well defined and uniform as in laminates manufactured by RTM.

### ***Solid Free-Form Fabrication (SFF)***

Solid free-form fabrication (SFF) is a method of making shapes without molds. It is best known in its stereolithography forms as a method of rapid prototyping. In stereolithography a laser photopolymerizes successive thin layers of monomer to build up a solid object. Extrusion solid free-form fabrication was developed by the University of Arizona in collaboration with Advanced Ceramic Research (Tucson, AZ) (14). It functions essentially as a three-dimensional (3D) pen plotter. In this case, a slurry is extruded by a stepper motor pushing on a syringe and forcing the material through a needle. By moving the syringe over a computer-controlled path, nearly any geometry can be created (Fig. 7.4). Advantages are that this method has the potential to produce new materials and complex composites that could not be made in any other way, for example, objectives with loose enclosed parts (a ball in a box). A typical procedure for formation of soy composites using SFF is given below.



**Fig. 7.4.** Sketch of the extrusion free-form fabrication apparatus.

## ***Solid Free-Form Fabrication of Soy Composites***

ESO and Epon 828 resin are mixed thoroughly in the weight ratio of 1:0.3. The mixture is mixed with Aerosil R805 and fibrous fillers. A vacuum is applied to remove air bubbles. The fiber-filled slurries show a yield point, such that formed parts hold their shape until cured. A curing agent, diethylenetriamine (DETA), triethylenetetramine, 60% tech (TETA), or Jefamine EDR 148 is added and the paste is placed into a 20-mL plastic syringe. Bars 75 mm × 8 mm × 4 mm were formed by deposition of five layers, subsequently cured at higher temperature for some time depending on the curing agent used. Solid free-form fabrication is conducted using an Asymtek model 402 fluid dispensing system, equipped with small stepper motors (Oriel stepper mike) to drive the delivery syringe. The Asymtek and syringe are controlled by a program written in Microsoft Quick Basic. Solid bar samples are written as a series of lines.

## **Characterization of Soy Composites Developed by SFF**

### ***Mechanical Testing***

The mechanical property testing is done using a 3-point bend test method with an Instron model 1100. The standard formula for the modulus,  $E$  and strength,  $\sigma$  in 3-pt bending of a beam was used:

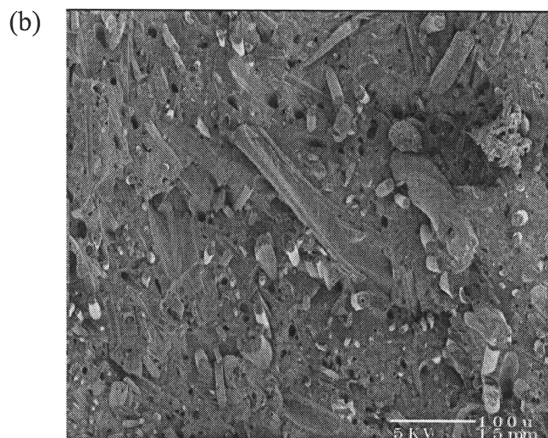
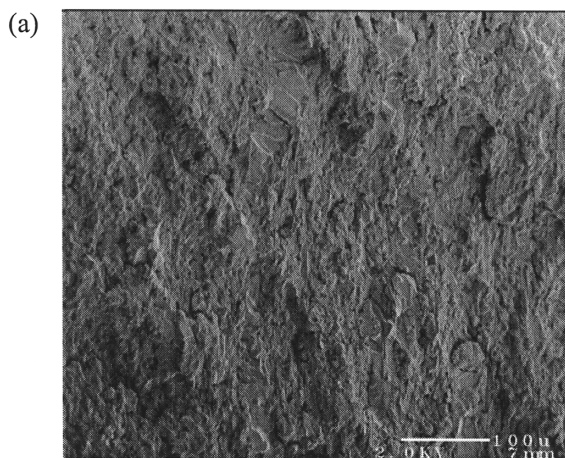
$$E = PL^3 / 4bd^3 \delta, \sigma = 3PL / 2bd^2$$

where  $P$  is equal to the break load,  $L$  is the support span,  $\delta$  is the deformation at the center under load  $P$ ,  $d$  is the sample height, and  $b$  is the sample width.

### ***Composite Morphology***

Scanning electron microscopy (SEM) is performed to characterize the morphology of soy composites. Figure 7.5 shows the SEM of a freshly fractured surface for soy composites filled with (a) Franklin Fiber<sup>®</sup> H-45 fiber, and (b) carbon fiber. They clearly indicate that the interfacial adhesion between the fiber and matrix is fairly good. This can be readily seen from the physical contact between the two components. The fibers are broken up from the matrix. However, holes and spacing occur along the fiber, resulting in poor contact and inferior stress transfer between the phases. The use of a combination of glass or carbon fiber with mineral fiber in thermoset matrix was investigated recently by Peng (15). The experimental results show that the use of different fiber types combined in testing bars tends to yield a higher flexural modulus compared with the single type fiber-epoxy composites at same conditions. Liu *et al.* (16,17) reported the studies of single-fiber and fiber combination reinforced soy composites. An example of using a fiber combination is the use of short milled glass fibers (1/32 in) with Franklin Fiber, H-45, as well as short carbon fibers with Franklin Fiber, H-45. Table 7.3 shows that the moduli





**Fig. 7.5.** Scanning electron microscope (SEM) photomicrograph of the freshly fractured surface of soy-based composites filled with (a) Franklin fiber and (b) carbon fiber.

of the composites increase compared with single type fiber-epoxy composites under the same conditions. SEM of the fractured surfaces of the composites after the flexural test are shown in Figure 7.6 (a) and (b). The near absence of holes around the fibers resulted in good contact between the phases. A combination of two fibers can be used to achieve composites with higher strength and stiffness properties than can be obtained with a single fiber type.

### ***Influence of Fiber Orientation on Flexural Modulus***

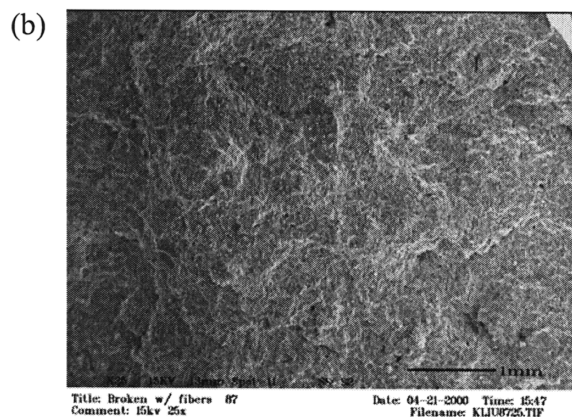
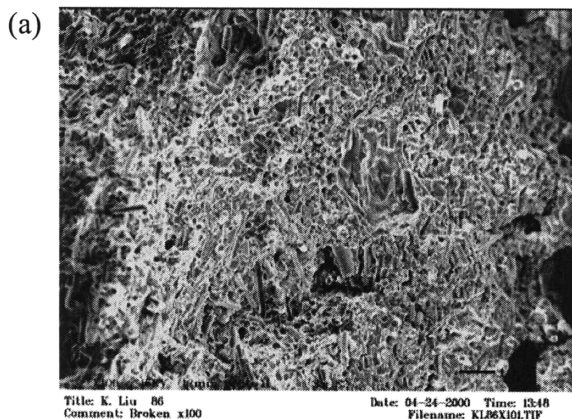
The high degree of alignment has a great influence on the properties of a composite. Peng *et al.* (18) reported in glass fiber/epoxy composites, 90% of fibers are within 10° of the machine write direction, measured by microscopy of a polished section. By writing a series of test bars with write axes at different angles to the

**TABLE 7.3**

Mechanical Properties of Free-Formed ESO/Epon/TETA or ESO/Epon/DETA with 32 vol% of E-Glass Fiber, 4.8 vol% Franklin Fiber<sup>®</sup> H-45<sup>a</sup>

Curing agent	Fiber 1	Fiber 2	Flexural strength (MPa)	Flexural modulus (GPa)	Strain at break (%)
TETA	Glass	Franklin	110.0	6.3	1.9
TETA	Carbon	Franklin	96.3	5.48	2.1
TETA	Glass	—	69.0	4.1	1.8
TETA	Carbon	—	63.0	3.6	2.4
DETA	Glass	Franklin	104.3	5.5	2.3
DETA	Carbon	Franklin	86.0	4.7	2.6

<sup>a</sup>Abbreviations: ESO, epoxidized soybean oil; TETA, triethylenetetramine; DETA, diethylenetriamine.



**Fig. 7.6.** Scanning electron microscope (SEM) photomicrograph of the freshly fractured surface of soy composites filled with the fiber combinations (a) E-glass fiber and Franklin fiber and (b) carbon fiber and Franklin fiber.

**TABLE 7.4**

Effect of Orientation on Epoxidized Soybean Oil (ESO)/Epon/Jeffamine EDR-148 Reinforced with 23.4 wt% Franklin Fiber<sup>®</sup> H-45

Fiber orientation	Flexural modulus (GPa)	Flexural strength (MPa)	Strain at break (%)
0	0.97	21.0	2.2
30	0.42	14.0	5.0
45	0.34	16.0	5.0
60	0.32	22.0	4.3
90	0.29	8.1	2.2

long axis, they can vary the modulus by approximately a factor of 3. Therefore test bars from ESO/Epon/Jeffamine EDR 148 reinforced with 23.4 wt% of Franklin Fiber<sup>®</sup> H-45 are made by writing at varying angles relative to the axis of the test bars. The modulus can be varied by a factor of  $\sim 3.5$  at writing angles parallel to the long axis than cross to the long axis (Table 7.4). This is significant because the composite modulus is at least as sensitive to orientation as it is to the fiber aspect ratio and volume fraction.

## Summary

Among the various composite molding methods, the solid free-forming method has the potential to produce new material and complex composites that could not be formed by other methods. Fiber-reinforced soy composite materials of high strength and stiffness can be formed by the free-form fabrication method. The higher strength and stiffness of soy composites can be achieved by a combination of two fibers. The fiber orientation follows the direction of motion of the write head that deposits the resins and has a large influence on the properties of the composite. These composite materials may be of great environmental interest because they comprise a high amount of agricultural resources. These can be used in agricultural equipment, the automotive industry, civil engineering, marine infrastructure, and the construction industry.

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