

## FILLER IN MATERIALS COMBINATIONS

### 16.1 BLENDS, ALLOYS AND INTERPENETRATING NETWORKS<sup>1-31</sup>

Polymer blends and alloys have more complex behavior in the presence of fillers than the binary mixtures of polymer and filler. The same factors, such as filler distribution, filler-matrix interaction, filler-matrix adhesion, particle orientation, nucleation, chemical reactivity, etc. have influence on properties, but this influence is complicated by the fact that there are two or more polymers present which compete for the same filler particles. These complex interactions result in many interesting phenomena discussed below.

The general idea behind polymer blending is to fulfill expectations that two different polymers, having different sets of properties, may contribute their most advantageous features to form product which surpasses properties of individual polymers. This expectation is rarely fulfilled in relation to mechanical properties because most polymer pairs are immiscible and do not have sufficient adhesion between phases. Two strategies are thus applied to find satisfactory materials: compatibilization and use of filler. In the case of compatibilization, a third component is added (most frequently block copolymer, having building blocks of both polymers, or the product of grafting of one polymer with introduced functional groups reactive towards the other polymer). This addition of the third component gives a relatively simple system in which polymers of the blend are still not mixed but are connected at interfaces through this third component. The comparison of this type of compatibilization to addition of filler compatibilized system is fairly simple. The addition of filler offers combinations given in Figure 16.1 These numerous possibilities of interaction can still be increased by the addition of compatibilizers having different interactions with polymers and fillers or by the use of combinations of fillers or both.

The above description stresses either chemical reactions in these combinations or physical interactions between components. In reality there is still additional effect which may induce changes to structure and thus properties. It is a commonly known effect of fillers on the nucleation of polymers. It can be perceived that filler does not affect nucleation of both polymers with the same intensity. In addition, the availability of polymers at the interface with fillers depends on various parameters such as viscosity, acid/base interaction, etc. If these two are included in the number of combinations, there is a theoretical abundance of possible combinations and thus

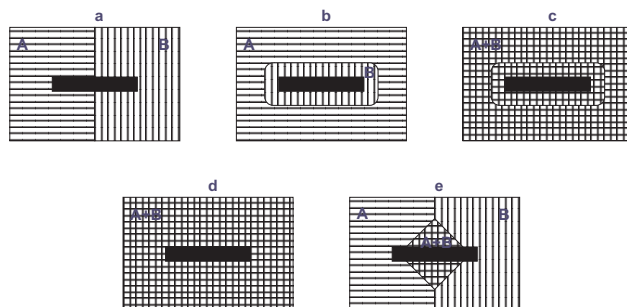


Figure 16.1. Models of interaction of a two component blend with filler. (a) polymers immiscible but both interacting with filler; (b) polymers immiscible but polymer B interacting with filler; (c) polymers miscible but only polymer B interacting with filler; (d) polymers miscible and both interacting with filler; (e) polymers immiscible but both interacting with filler forming a miscible interphase on the surface of filler. [Modified based on Persson A L, Bertilsson H, *Composite Interfaces*, **3**, No.4, 1996, 321-32.]

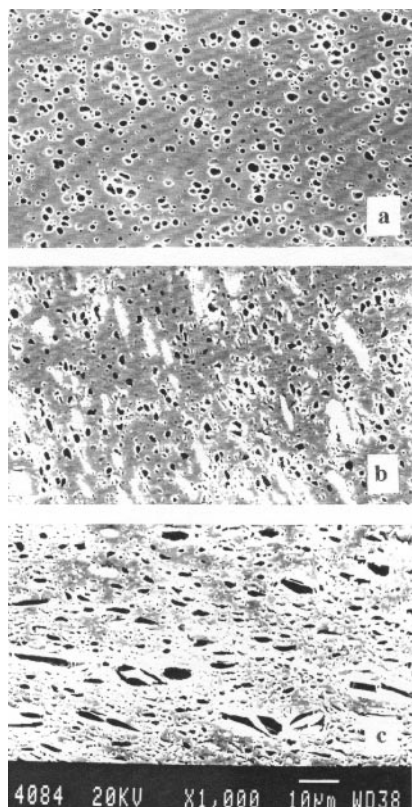


Figure 16.2. SEM photographs of PP/EP blends. (a) PP/EP blend; (b) PP/EP/talc blend with separated microstructure; (c) PP/EP/talc blend with core-shell microstructure. [Adapted, by permission, from Shanks R A, Long Y, *Polym. Networks Blends*, **7**, 1997, 87-92.]

properties with real solutions are always based on combinations of several model patterns. The participation of each idealized component model structure is influenced by the process conditions. Further information on this subject can be found in the expert monographic source.<sup>32</sup>

Figure 16.2 shows examples of morphology of PP/EP blends containing talc.<sup>33</sup> The separated microstructure was obtained by mixing PP, PP grafted with maleic anhydride, and filler, followed by adding EP. In the separated microstructure the dark holes (micrograph b) are EP particles and talc particles are the brightest fragments. The shapes of core-shell particles are random because they depend on the shape of encapsulated particles. Further observations from this study are discussed below.<sup>33</sup>

This abundance of possibilities, combined with still large experimental difficulties in distinguishing between the numerous interactions and morphologies, creates opportunities more for the future than for today's benefit. The existing information is still on the very initial stage of understanding. Inverse gas chromatography was used to explain why, in polyamide-6/SAN blends,

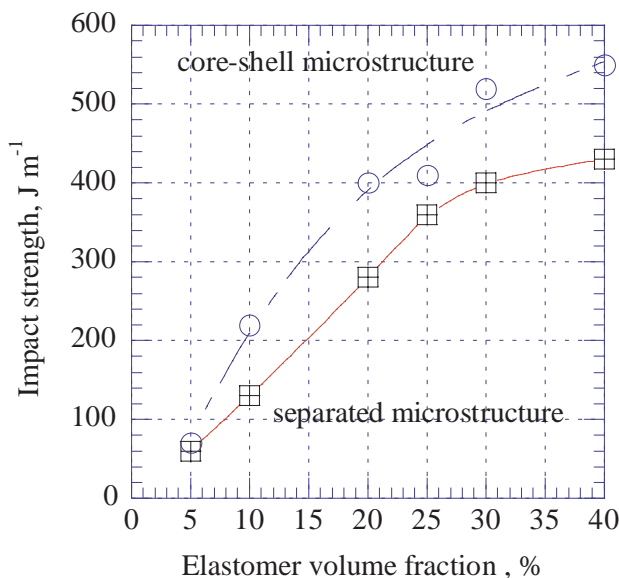


Figure 16.3. Impact strength vs. EP content for PP/EP blend containing 15 wt% talc. [Adapted, by permission, from Shanks R A, Long Y, *Polym. Networks Blends*, 7, 1997, 87-92.]

polyamide-6 interacts with aluminum borate whiskers. The interaction is believed to be a result of the Lewis acid/base properties of filler and polymers.<sup>25</sup>

Two rubbers – natural and butadiene – were mixed in different proportions and reinforced with cellulose fiber.<sup>26</sup> The results show that the proportion between rubber and fiber content are essential parameters determining tensile strength. The relationships between tensile strength and cellulose content are different for various proportions of both rubbers. The information includes the results of mechanical testing which is not sufficient to uncover the reasons for these different relationships. Factorial experimental design was used to elucidate the effect of compatibilizer, different polymers and fillers. The results of testing about 50 combinations allowed the conclusion that graphite acts as reinforcing agent.<sup>27</sup>

Figure 16.3 shows the effect of core-shell microstructure and separated microstructure on the impact strength of filled blends. Blends containing core-shell structures always give better performance. Figure 16.4 shows the influence of EP on the effect of filler on impact strength. With increasing EP concentration, impact strength increases, but at the same time impact strength becomes increasingly more sensitive to the filler content.<sup>33</sup>

Polymers such as poly(vinylidene fluoride) and polystyrene form incompatible blends.<sup>6</sup> Compounding with copper particles and carbon black affects changes in the morphology of the blends. Both fillers change the crystalline geometry of PVDF. The increase in the amount of copper particles increases the crystallization rate. With carbon black, the crystallization rate initially decreases to increase again at higher loadings, but generally there is no gain compared with unfilled polymer.

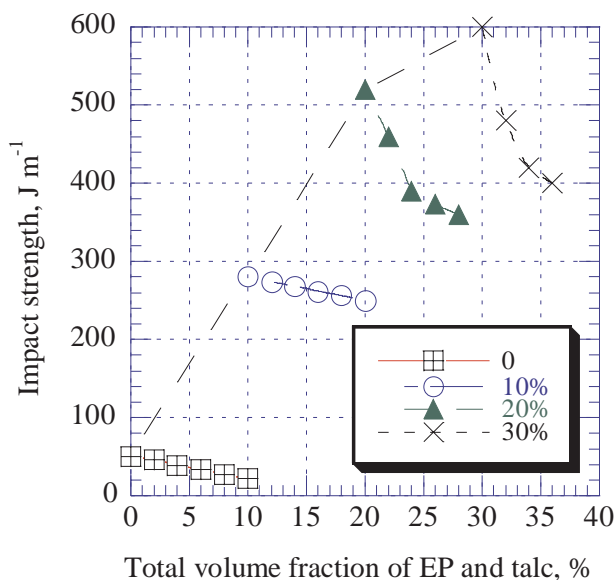


Figure 16.4. Impact strength vs. volume fraction of EP and filler for PP/EP blends. [Adapted, by permission, from Shanks R A, Long Y, *Polym. Networks Blends*, 7, 1997, 87-92.]

The phase morphology is modified by both fillers which help to micronize and homogenize both phases. Carbon black, in addition, acts as a compatibilizer, which is seen from shifts in the glass transition temperatures of both polymers and in a decrease in melting point of PVDF.<sup>6</sup>

It is not only the blend morphology which is affected by filler presence; filler orientation might be affected by its surface treatment, as was observed in the works on PC/ABS blends containing aluminum borate whisker.<sup>7</sup> When the whisker surface was treated with epoxy silane, its reaction to flow in injection and compression molding processes changed, resulting in a different orientation even though all other parameters of process and composition were the same.<sup>7</sup>

A small addition of talc (8 wt%) changes fatigue resistance. Figure 16.5 shows that crack initiation is delayed (marked in the figure), but crack propagation is the same. The work dissipated has formed the same relationship with crack length for the filled and unfilled samples, but the energy release rate and resistance moment were slightly higher for filled material.<sup>8</sup>

The method of filler incorporation also determines its distribution between the phases.<sup>10</sup> When PE/TPU blend was in the molten state when mixed with carbon black, the island morphology was obtained with carbon black mostly resident in one phase. Mixing at room temperature followed by cold molding (50°C) resulted in the mixture with uniformly distributed carbon black.<sup>10</sup>

The introduction of reactive components during blend formation further increases the complexity of the process and affects results. Polypropylene functional-

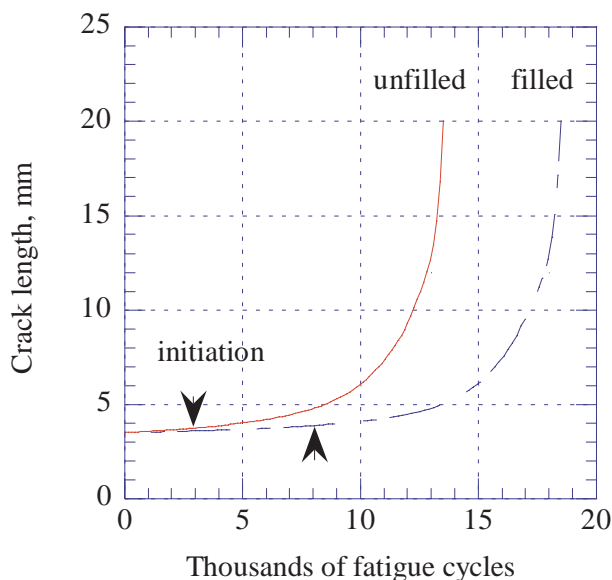


Figure 16.5. Crack length vs. the number of fatigue cycles for PC/ABS blends filled with 8 wt% talc and unfilled. [Adapted, by permission, from Seibel S R, Moet A, Bank D H, Nichols K, Antec '93. Conference Proceedings, New Orleans, La., 9th-13th May 1993, Vol. I, 902-5.]

ized with maleic anhydride was used to compatibilize a blend of polypropylene with polyamide-6 in the presence of glass beads. The kinetics of two processes was important: blend compatibilization and filler encapsulation. The process of blend compatibilization is slower than filler encapsulation. This restricts addition order allowing the blend to compatibilize first, followed by the addition of filler to the already compatibilized blend.

In blends composed of immiscible polymers, amorphous polymer does not affect the crystallization of crystallizable polymer, but if two polymers are miscible, amorphous polymer acts as diluent and affects crystallization of the second polymer. Poly( $\epsilon$ -caprolactone) is a crystallizable component of the blend with poly(vinyl butyral), which is studied in compositions containing carbon black.<sup>2</sup> Typically, blends of these two polymers form very large spherulites, and it is interesting to find out how carbon black affects crystallization and other properties of the blend as well as the distribution of carbon black in relationship to the spherulites. Figure 16.6 shows that spherulite growth rate is independent of carbon black presence (points of carbon black filled and carbon black free blend follow the same relationship). Additional data show that crystallization rate decreases with the amount of PVB increasing.<sup>2</sup> Carbon black aggregates are mainly found in spherulites.

Conducting polymers based on carbon black should contain a small amount of carbon black to facilitate processing. To reduce the amount of carbon black, one must create inhomogeneity in the material either by using the system which rejects carbon black from the crystalline region (opposite to the PCL/PVB blend above) or

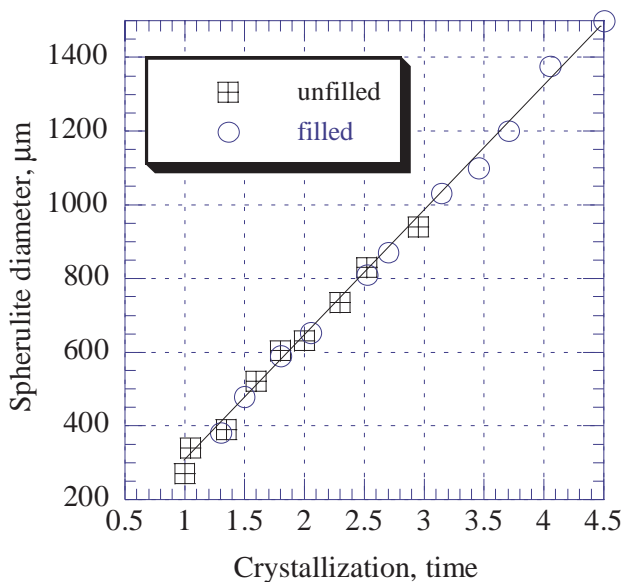


Figure 16.6. Spherulite diameter vs. crystallization time for PCL/PVB blend with (5 wt%) and without carbon black. [Adapted, by permission, from Lee J-C, Nakajima K, Ikehara T, Nishi T, *J. Appl. Polym. Sci.*, **64**, 1997, 797-802.]

by the use of an immiscible blend in which carbon black resides in the minor phase or, better, in the interphase.<sup>3</sup> Two conditions must be fulfilled for a blend to have conductivity at a low concentration of carbon black: heterogeneous distribution of carbon black and adequate phase morphology. Two phase morphologies support this goal: one polymer forms a continuous phase containing carbon black, or both polymers have cocontinuous morphologies and carbon black particles are possibly located in the minor phase. The aim of one study was to use the cocontinuous morphology of a PE/PS blend to improve conductivity.<sup>3</sup> Addition of carbon black was found to increase the continuity fraction from the range of 30 to 45 wt% PE to the range from 50 to 65 wt%. This can only be achieved if carbon black has either interfacial activity or a kinetic effect on the coalescence process. Based on image analysis results, it was concluded that carbon black prevents phase coalescence. The blends containing carbon black were stable during prolonged thermal treatment (24 h at 200°C). Figure 16.7 shows that controlled annealing may help to improve blend conductivity even further since only 0.4 wt% carbon black is needed if either annealing time or temperature are increased. These results suggest that in the region of cocontinuity, carbon black was localized at the interface. Further efforts of this work concentrated on the selective localization of carbon black at the interface by regulating the molding temperature.<sup>11</sup> Figure 18.4 shows the results for a carbon black filled blend of PS/PIP. The results are essentially similar to those given by Figure 16.7, pointing at process temperature as an important factor modifying the distribution of carbon black.

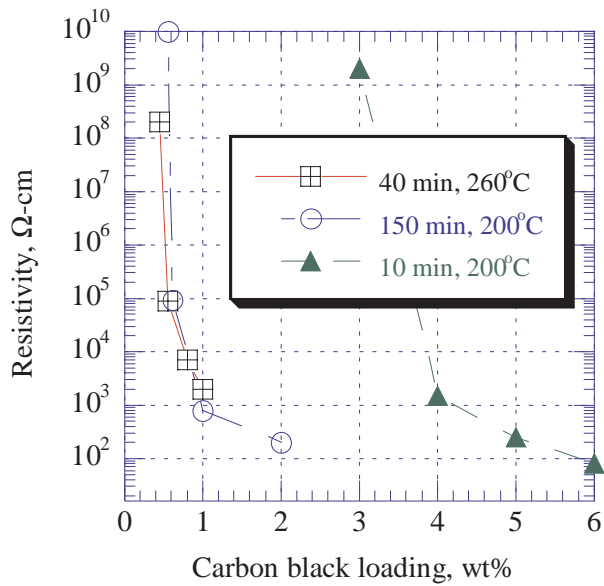


Figure 16.7. Resistivity vs. carbon black content in a PE/PS blend, depending on annealing regime. [Adapted, by permission, from Gubbels F, Blacher S, Vanlathem E, Jerome R, Deltour R, Brouers F, Teyssie Ph, *Macromolecules*, **28**, No.5, 1995, 1559-66.]

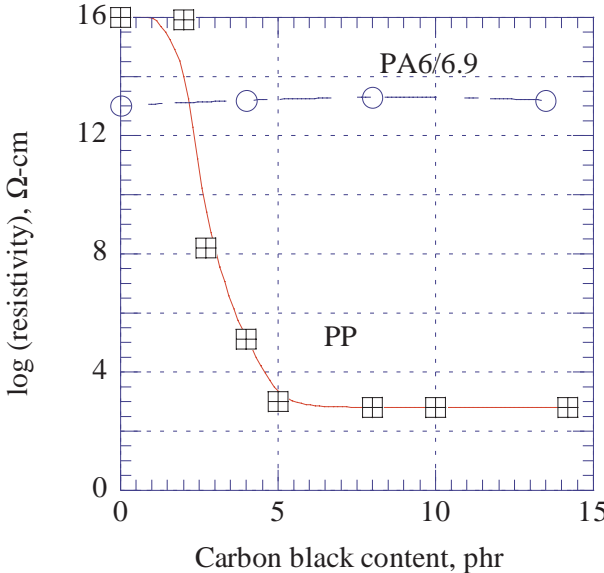


Figure 16.8. Resistivity vs. carbon black content. [Adapted, by permission, from Tchoudakov R, Breuer O, Narkis M, Siegmann A, *Polym. Engng. Sci.*, **36**, No.10, 1996, 1336-46.]

The polymers included in the polymer blend have impact on the development of conductivity behavior. Figure 16.8 shows that carbon black rapidly reduces the resistivity of polypropylene at about 2.5 phr whereas the conductivity of polyamide

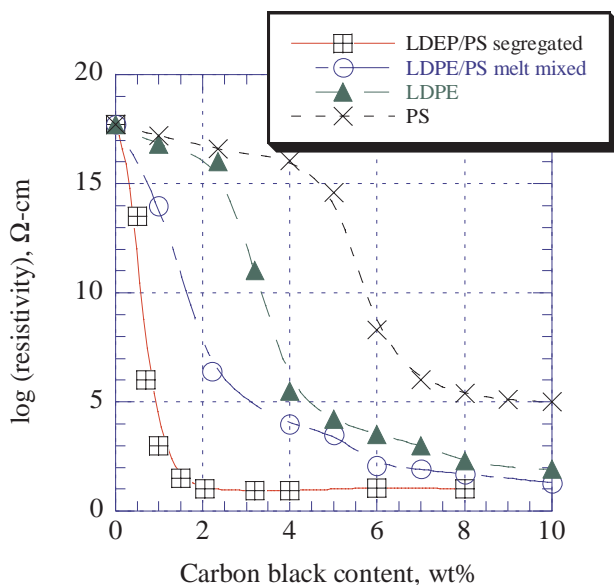


Figure 16.9. Resistivity vs. carbon black content for polymers and blends. [Adapted, by permission, from Kozłowski M, *Polym. Networks Blends*, **5**, 1995, 163-172.]

is not affected in the range of carbon black concentration. At the same time, polyamide has a much higher affinity to carbon black, which is demonstrated by the fact that even if carbon black is first added to polypropylene, carbon black is transferred to polyamide. Mixing of these two polymers with carbon black gives higher resistivity with increasing concentration of polyamide, since carbon black does not influence its conductivity to a great degree.<sup>20</sup> Polycarbonate has a similar characteristic in mixtures with carbon black and polypropylene, but the sudden decrease in conductivity occurs around 5 phr.<sup>24</sup> Polycarbonate, similar to polyamide also has a much stronger affinity to carbon black than polypropylene. Carbon black is thus localized in the polycarbonate phase which is distributed in polypropylene. With a small content of polycarbonate in the blend (up to 30 wt%), carbon black becomes concentrated in polycarbonate phase and resistivity rapidly decreases.<sup>24</sup>

Figure 16.9 compares the effect of carbon black concentration on PS, LDPE, and their blends. The polymer blends have better conductivity than individual polymers. A rapid decrease in conductivity by small additions of carbon black can be obtained in segregated blends, but mechanical properties of such blends are inferior.<sup>34</sup>

The blend morphology containing conductive filler (e.g., carbon black) was simulated by the model based on Cahn's approach. Figure 16.10 shows the two-dimensional cut explaining the localization of carbon black between two incompatible phases, and Figure 16.11 shows the effect of carbon black concentration on the prediction of conductivity.<sup>15</sup> This simple model of interfacial film partitioning



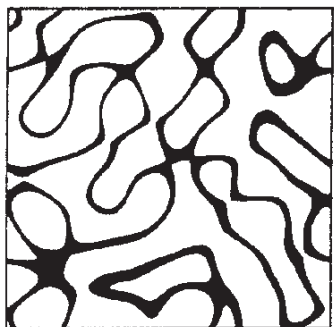


Figure 16.10. Model morphology shown by two-dimensional cut for carbon black filled blend. [Adapted, by permission, from Knackstedt M A, Roberts A P, *Macromolecules*, **29**, No.4, 1996, 1369-71.]

in two polymer phases gives a conductivity exponent in agreement with experiment.<sup>15</sup>

Interpenetrating networks experience different effects of filler incorporation because of the method of their formation and the higher probability of chemical bond formation with fillers due to the reactivity of the system. There are also more regulating factors because of the larger number of components, which affect properties through different sequences of incorporation. One example of improvement is given in Figures 19.23 and 19.24 which show that mica affects damping characteristics of interpenetrating networks.<sup>9</sup> An interpenetrating network composed of polypyrrole and EPDM

containing fillers was used to show that conductive materials can be obtained by incorporation of an intrinsically conductive polymer. Fillers such as silica and kaolin were used to improve mechanical properties which are affected by formation of interpenetrating network.<sup>18</sup>

The microphase separation of a semi-interpenetrating network based on polyurethane and poly(epoxy isocyanurate) containing  $\text{Fe}_2\text{O}_3$  was studied by dynamic mechanical spectroscopy. The preferential absorption of polyurethane on

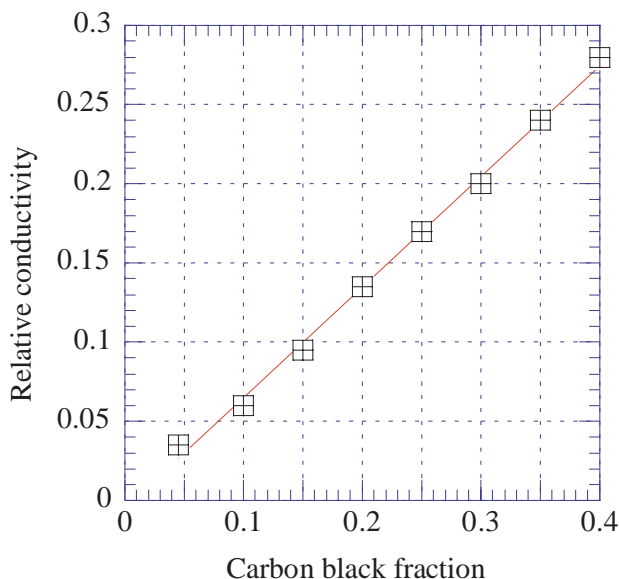


Figure 16.11. Conductivity of simulated blend vs. carbon black fraction. [Adapted, by permission, from Knackstedt M A, Roberts A P, *Macromolecules*, **29**, No.4, 1996, 1369-71.]

filler causes microphase separation.<sup>30</sup> The properties of an epoxy-silica interpenetrating network are discussed.<sup>31</sup> The unique morphological properties can be obtained by network formation, which cannot be obtained by component mixing. Thermal properties such as stability and char yield are substantially improved by network formation.

The above review of current findings shows that polymer blending in the presence of fillers may offer interesting new products. Considerable effort was made in the studies of conductive polymers, and many valuable practical results are available. The effect of fillers on the improvement of mechanical properties is still on the exploratory stage. At the same time, numerous theoretical possibilities exist which should contribute to improved materials in the future.

## 16.2 COMPOSITES<sup>35-62</sup>

One definition describes the composite material as follows: "A material created by the synthetic assembly of two or more materials (a selected filler or reinforcing element and compatible matrix binder) to obtain specific characteristics and properties." Composites began from the idea to replace metals with materials which can match their strength but do not corrode, are lighter, and less expensive. Because these goals were realized in the early days by using reactive glue and fiber, composites are generally thought of as fiber reinforced resins. The meaning today encompasses all fillers, and frequently the term composite is applied to any mixture of polymeric material and filler. With this broad definition, composites are the subject of entire books. In order to avoid repeating information, this discussion includes only some aspects of composites such as

- Mixtures of fibers and particulate materials
- Material design to obtain materials having certain combinations of properties

The remaining aspects of this large and complex group of materials are either found in various parts of this book or can be found in specialized monograph on the subject.<sup>32</sup> The major selection criteria of advanced composites are properties of the fibers or other reinforcing fillers, properties of the matrix, fiber-matrix interface, and processing technology, which combined, results in engineered properties.

There are numerous benefits of mixing the elongated and spherical particles as established in the result of a broad study.<sup>61</sup> Figure 16.12 shows the effect of glass fibers, glass microspheres, and their mixtures on mechanical properties of polyamide-66. The data show that only unnotched Charpy impact test results are lower for the combination of glass fiber and microspheres than for any of the fillers alone. In addition to improvement of mechanical strength parameters, properties can be balanced to the requirement by changing the proportion of both fillers.<sup>61</sup>

The compositions of different fillers are easier to process. Figure 16.13 shows that replacement of part of calcium carbonate by microspheres results in reduction of viscosity.<sup>61</sup> Similar reduction of viscosity can be expected in the mixtures of fi-

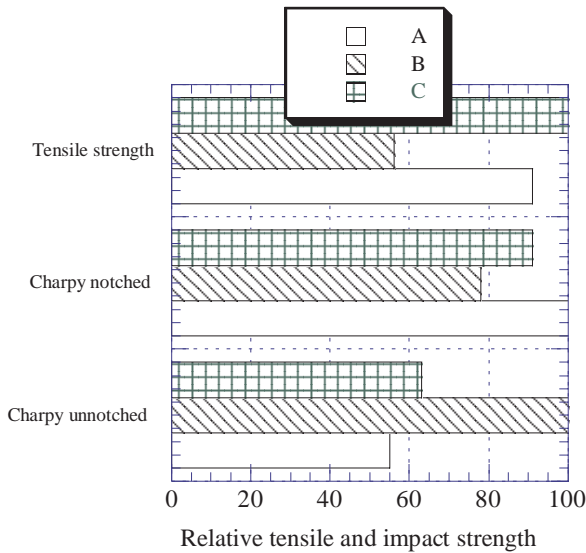


Figure 16.12. Relative values of mechanical performance for polyamide-66 reinforced with 15 wt% glass fiber (A), 15 wt% microspheres (B), and their combination of 15 wt% each (C). [Data courtesy of Abrasivos Y Maquinaria, SA, Barcelona, Spain]<sup>61</sup>

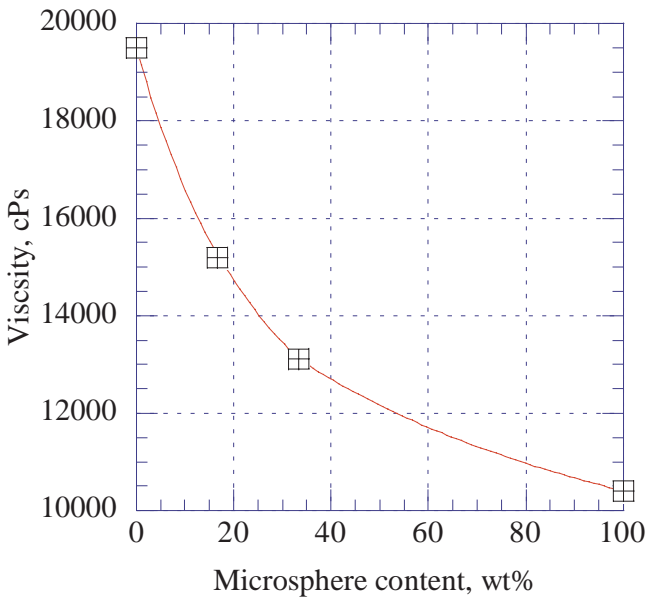


Figure 16.13. Viscosity of polyester resin filled with calcium carbonate and microspheres (total content of filler (CaCO<sub>3</sub>+microspheres) is 60 wt%). [Data courtesy of Abrasivos Y Maquinaria, SA, Barcelona, Spain]<sup>61</sup>

bers and microspheres because of their free flowing character. In injection molding, glass beads have ball-bearing effect which makes flow of material containing fiber much easier which results in lower temperature and shorter cycle.

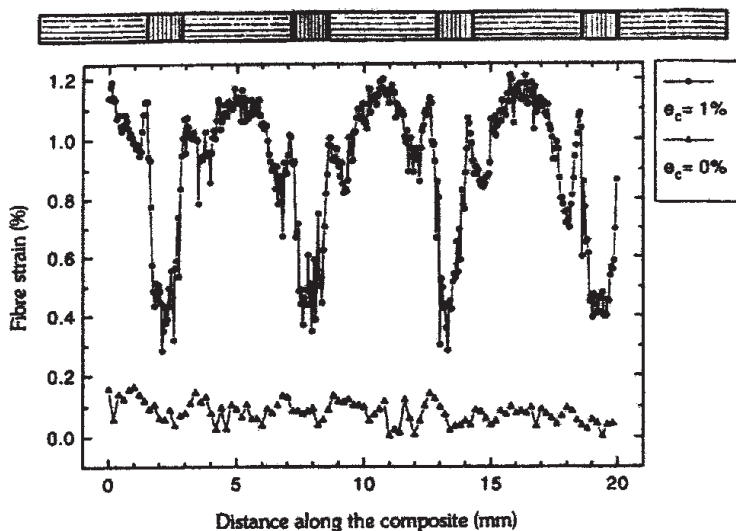


Figure 16.14. Fiber strain vs. distance along composite recalculated from stress-induced Raman band shifts. [Adapted, by permission, from Young R J, *Prog. Rubb. Plast. Technol.*, **11**, No.2, 1995, 124-36.]

Abrasion resistance and impact strength are improved simultaneously when a combination of beads and fibers is used. In these composites, glass beads dissipate energy and fibers protect beads from abrasion.<sup>61</sup>

The deformation of fibers under strain and strain distribution are important for the designer of composites. Figure 14.28 shows the Raman spectra of aramid fiber measured with and without the strain. There is a sufficient shift in spectral peaks to use it for the analysis of complex materials. This method was adapted for evaluation of epoxy resin reinforced with satin aramid fabric. Figure 16.14 shows the results along the warp face.<sup>39</sup> The schematic drawing above the graph shows positions of warp threads which match peaks on the Raman spectrum when the fabric is under strain. The entire strain applied to the composite is transferred to warp threads. This technique has excellent capabilities for mapping stress distribution in composites. Similar information was obtained along the weft face, but in this direction only 20 to 70% strain is transferred.<sup>39</sup>

Combination of several properties is becoming increasingly important in modern industry. One example may be taken from electronics, where in addition to mechanical properties and electric resistance, thermal stability and conductivity are important requirements. It was estimated that the increase of temperature by 10°C reduces time to failure by the factor of two.<sup>40</sup> A finite analysis model was developed which accounts for the following properties of filled composites: microstructure, effect of particle shape, formation of conductive chains, effect of filler aspect ratio, and interfacial thermal resistance. The predictions of the model indicate the most

advantageous dispersion of particles in the matrix. Conductive chain formation, merging of conductive chains, branching of conductive chains, and agglomeration at the center give effective thermal conductivities of 1.33, 1.24, 1.16, and 0.73 W/m·K, respectively.<sup>40</sup>

Achieving a combination of several mechanical properties is also a frequent problem. The addition of fillers to composites improves their strength, modulus, and shrinkage, but toughness of the composite is usually reduced. If elastomer is added to the composite, toughness is improved but stiffness decreases. A model was developed in which improvement of all these properties is examined by the application of core-shell fillers. The use of core-shell filler based on carbon black resulted, according to the proposed model, in a composite which had high strength, toughness, and modulus.<sup>49</sup>

Varistors are electric components with variable resistance, depending on the electric current. Varistors should have low breakdown field strength combined with fairly high non-linearity of electrical conductivity. Special varistor powdered filler was prepared to obtain these properties.<sup>53</sup>

Aramid fibers are popular in the reinforcement of various matrix materials. It is frequently the case that low water uptake by a composite is required, which cannot be regulated by the matrix. Figure 16.15 shows that aramid fibers differ in water sorption kinetics. Fiber E gives better performance due to a hydrophobic coating. This lower water sorption of the fiber decreases water sorption of the composite, as was established in the study.<sup>58</sup>

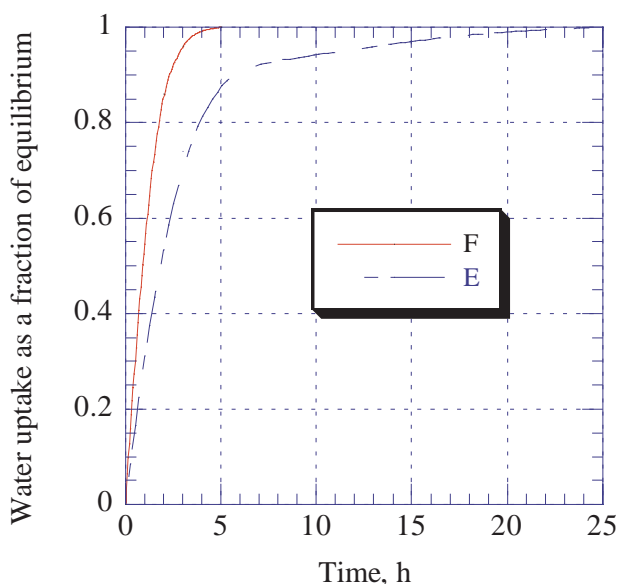


Figure 16.15. Water sorption kinetics of aramid fibers vs. time. [Adapted, by permission, from Rebouillat S, Escoubes M, Gauthier R, *J. Adhesion Sci. Technol.*, **10**, No.7, 1996, 635-50.]

Fire proofing of various composites is an important example of design to introduce material having a certain set of other required properties combined with fire resistance. This is usually a difficult task, considering that fire retarding fillers must be usually used in large quantities, and this deteriorates mechanical properties and makes processing more difficult because of increased viscosity. Such technologies are developed to obtain fire resistant materials which offer good mechanical performance.<sup>59,60</sup>

Considering that properties of the composite depend on filler, matrix, and their adhesion, an interesting proposal was put forward.<sup>56</sup> The so-called matrix or template polymerization was proposed for tailoring the properties of composites. This method allows polymer to grow on organic or inorganic matrices by initiation of polymerization on the surface of the matrix. The polymers produced on matrices frequently have very different properties than polymers obtained without the effect of a template because template changes the configuration and conformation of polymers. The other advantage of template polymerization is in changing reactivity, considering that monomers without template have a different conformation which may hinder the chemical reaction. Introduction of a template may change access to reactive groups and thus change kinetics of the reaction. The study of template polymerization is an interesting field but the findings were not applied in practice because of difficulties in separating the obtained polymer from template. In the area of the composite, this curse may become a blessing since difficulty of separation frequently means excellent adhesion. Some works on nanocomposites apply these methods. More information on template polymerization can be found in the first monograph recently published on this subject.<sup>62</sup>

### 16.3 NANOCOMPOSITES<sup>63-91</sup>

These novel materials receive increasing interest because of their complex structure and interesting performance characteristics. The following points will be discussed here:

- Nanocomposite design and formation
- Resultant particle size
- Potential applications
- Properties

Nanocomposites, in addition to small particle sizes usually are required to have a very uniform composition. These two requirements impose constraints on the methods of synthesis. In addition, the required form of the final product is given consideration in the choice of the method of their synthesis. These constraints resulted in numerous design strategies in methods of nanocomposite manufacture, discussed below.

One method is to produce particulate material of the required size and then to incorporate it in castable matrix, followed by film formation. Figure 16.16 shows the chemistry of the process and the steps from the raw materials to the final film

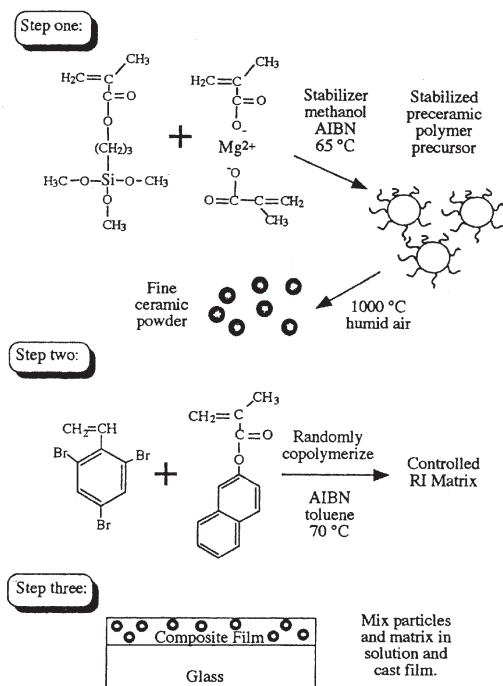


Figure 16.16. *Ex situ* synthesis of optical composite for laser amplifying films. [Adapted, by permission, from Beecroft L L, Ober C K, *Chem. Mater.*, **9**, 1997, 1302-17.]

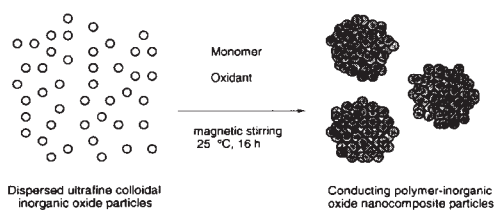


Figure 16.17. Particulate nanocomposite formation. [Adapted, by permission, from Maeda S, Armes S P, *Synthetic Metals*, **73**, 1995, 151-155.]

used for amplification in lasers.<sup>63</sup> In the first stage, a polymer based on silicon and magnesium containing monomers is produced, resulting in beads having sizes of 100-500 nm. These beads are subjected to the treatment at 1000°C, where the organic part is removed and crystalline fosterite is formed, having 100 nm size of beads. In optical applications, if particles are larger than 25 nm, it is very important to select a polymer for the matrix which has a very similar refractive index (refractive index mismatch less than 0.02); otherwise, optical scattering will be experienced. The polymer used in step two was selected for a precise match of refractive index.

Figure 16.17 shows the formation of conductive polymer/inorganic oxide nanocomposite particles. Silica, having a particle size of 20 nm, was dispersed in water, oxidant was added, followed by addition of monomer (pyrrole or aniline), and polymerization was conducted under constant stirring for 16 h at room temperature. “Raspberry” clusters of nanocomposite were obtained.<sup>70</sup>

Silicon nanoparticles in a narrow range of sizes (25-50 nm) were obtained by mechanical attrition.<sup>74</sup>

This simple method of production of particles in large quantities may find a broad range of applications.

The development of nanocomposites containing metal particles may be very rewarding since such materials can be useful in catalysts, an optical and electronic devices.<sup>79</sup> Figure 16.18 shows the schematic diagram of the method of synthesis. The polymers used in this material were poly(4-methyl-1-pentene) and poly(tetrafluoroethylene). Dimethyl(cyclooctadiene)platinum(II) was used as the metal precursor. The metal precursor was dissolved in supercritical liquid carbon dioxide

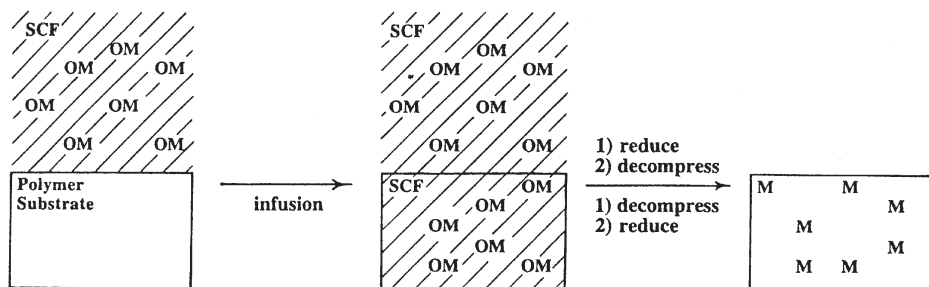


Figure 16.18. Schematic diagram of the synthesis of a polymer/metal nanocomposite. [Adapted, by permission, from Watkins J J, McCarthy T J, *Chem. of Mat.*, **7**, No.11, 1995, 1991-4.]

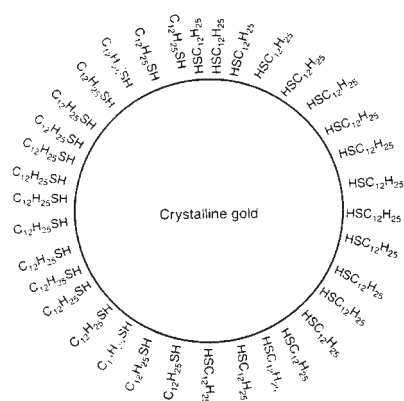


Figure 16.19. Thiol-derivatized nanometric gold. [Adapted, by permission, from Gonsalves K E, Carlson G, Chen X, Kumar J, Aranda F, Perez R, Jose-Yacamán M, *J. Mat. Sci. Lett.*, **15**, No.11, 1996, 948-51.]

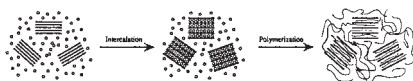


Figure 16.20. Layered composite synthesis. [Adapted, by permission from Messersmith P B, Giannelis E P, *Chem. of Mat.*, **5**, No.8, 1993, 1064-6.]

*N,N'*-dimethylacetamide, followed by film casting, and reduction of metal salts by sodium borohydrate.<sup>210</sup> The metal particle size depended on metal salt and concentration.

The layered nanocomposites can be obtained as shown in Figure 16.20. Intercalation of  $\epsilon$ -caprolactone into the silicate galleries was done simply by suspending

and infused into solid polymers. In the next step, metal precursor was either chemically or thermally reduced to produce metal domains. The properties of supercritical carbon dioxide are very important here. It has a high permeation rate in all polymers. Neither polymer nor metal precursor need to be soluble in carbon dioxide. This gives a method which can be adapted to any system.<sup>79</sup>

Surface-functionalized gold particles were obtained by a phase-transfer reaction of gold ions with dodecanethiol. Figure 16.19 shows the structure of such particles.<sup>83</sup> These particles are of interest because they have nonlinear optical polarizability. The particles were mixed with MMA and initiator and polymerized. No agglomeration of particles was detected, but the polymerization rate in the presence of nanoparticles was inhibited.<sup>83</sup>

Metal-containing nanocomposites were obtained by dispersion of metal chlorides in polyurethane. Both polyurethane and metal salts were dissolved in



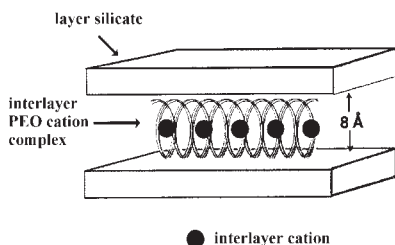


Figure 16.21. Schematic representation of layered nanocomposite with ion mobility. [Adapted, by permission, from Ruiz-Hitzky E, Aranda P, Casal B, Galvan J C, *Adv. Mat.*, 7, No.2, 1995, 180-4.]

silicate powder in the monomer.<sup>68</sup> In the next step, polymerization was conducted at 100°C, resulting in polymer-intercalated silicate embedded in a poly( $\epsilon$ -caprolactone) matrix. During intercalation, silicate spacing was increased by 12.8 to 14.6 Å. After polymerization, spacing was reduced to 13.7 Å, which is due to silicate layer thickness (9.6 Å) and interchain distance (4 Å). The polymer is strongly adsorbed onto the silicate layers and shows no melting transition.<sup>68</sup> Layered

nanocomposites derived from Na-montmorillonite had a regular lattice spacing of 17.7 Å, which is relative to twice the gallery expansion by two layers of polymer.<sup>69</sup>

Figure 16.21 shows structural arrangement of PEO intercalated into phyllosilicate (montmorillonite). Other organic components such as crown ethers can also be used. This is an example that ionic structures can be regularly located within the structure of the composite. These ionic structures can be useful in ion selective sensors.<sup>72</sup>

Vanadium pentoxide xerogels are very reactive layered host materials which can be intercalated by various means such as cation-exchange, acid-base chemistry, or redox reactions.<sup>77</sup> Vanadium pentoxide xerogel was prepared by polymerization of  $\text{HVO}_3$  after a few days of reaction at room temperature. The resultant xerogel

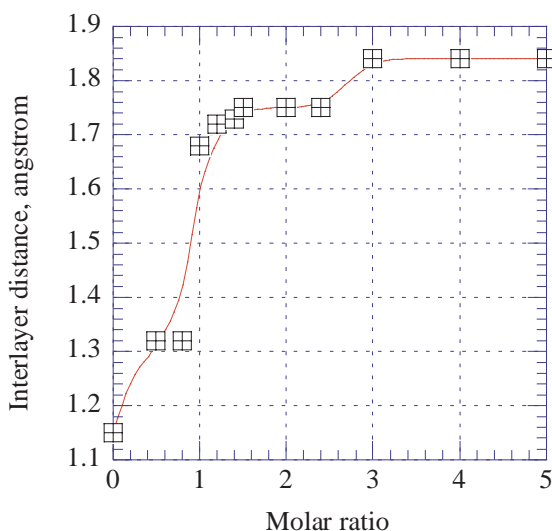


Figure 16.22. Interlayer spacing vs. molar ratio of PEO to  $\text{V}_2\text{O}_5$ . [Adapted, by permission, from Liu Y J, Schindler J L, DeGroot D C, Kannewurf C R, Hirpo W, Kanatzidis M G, *Chem. of Mat.*, 8, No.2, 1996, 525-34.]

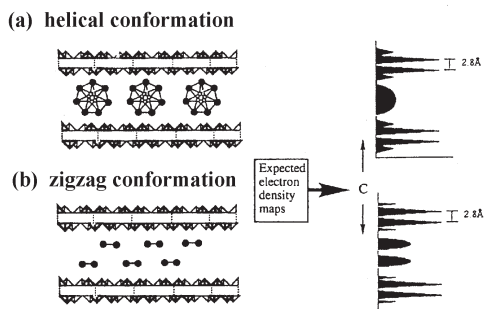


Figure 16.23. Schematic structures of PEO conformation in  $V_2O_5$  xerogel and their expected electron density projections along the  $c$  axis. (a) coil conformation, (b) zigzag conformation forming bilayer. [Adapted, by permission, from Liu Y J, Schindler J L, DeGroot D C, Kannewurf C R, Hirpo W, Kanatzidis M G, *Chem. of Mat.*, 8, No.2, 1996, 525-34.]

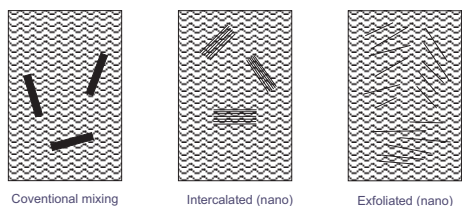


Figure 16.24. Three possible types of polymer/clay composites. [Adapted, by permission, from Lan T, Kaviratna P D, Pinnavaia T J, *Chem. of Mat.*, 7, No.11, 1995, 2144-50.]

was mixed with different molar ratios of PEO and cast into films after water evaporation at room temperature. The interlayer spacing depended on molar ratio as shown in Figure 16.22. Figure 16.23 shows some possible conformations of PEO chains and their expected electron density projections. It was determined that the bilayer model (b) is correct.

Figure 16.24 shows the schematic representation of dispersed clay particles in a polymer matrix.<sup>78</sup> Conventionally dispersed clay has aggregated layers in face-to-face form. Intercalated clay composites have one or more layers of polymer inserted into the clay host gallery. Exfoliated polymer/clay nanocomposites have low clay content (lower than intercalated clay composites which have clay content ~50%). It was found that 1 wt% exfoliated clay such as hectorite, montmorillonite, or fluorohectorite increases the tensile modulus of epoxy resin by 50-65%.<sup>78</sup>

Montmorillonite was used in a two stage process of nanocomposite formation.<sup>81</sup> In the first step, montmorillonite was intercalated with vinyl monomer and then used in the second step to insert polystyrene by *in situ* polymerization.

Electron behavior, optical properties, catalytic properties, conductivity, and magnetic properties of nanocomposites were discussed in an extensive review paper.<sup>73</sup> Complementary use of electron paramagnetic resonance and nuclear magnetic resonance helped to understand chain mobility in nanocomposites obtained from poly(ethylene oxide) encapped with triethoxysilicon.<sup>80</sup> This nanocomposite is composed of PEO chains attached to silica clusters. It was found that chain fragments close to the silica clusters have hindered mobility due to the reduction of local free volume. The length of this hindered segment is estimated as three ethylene oxide units.<sup>80</sup>

**Table 16.1. Particle size and applications of nanocomposites**

Filler	Matrix	Particle size, nm	Application	Ref.
Fosterite	Tribromostyrene/naphthyl methacrylate	100	optical composite for laser amplifying films	63
Silica	Polyaniline	200	marker particles in diagnostic assays	70
Aluminum nitride	Polyimide	20-100	gas barrier, low thermal expansion	71
Phyllosilicate	Polyethylene oxide	layered	solid electrolyte, ion-selective materials	72
Silicon	-	25-50	nanoparticles for any application	74
Vanadium pentoxide	Polyethylene oxide	layered	-	77
Montmorillonite	Epoxy resin	layered	reinforcement	78
Platinum	PTFE	15	optical, electronics	79
Montmorillonite	Polystyrene	150-400	combination of high strength and high toughness	81
Smectite	polypropylene	layered	polymer reinforcement	82
Gold	PMMA	6-14	nonlinear optical devices	83
Cellulose whisker	St-BuAc-copolym.	n/a	polymer reinforcement	84
Metals (Fe, Co, Ni, Cu)	Polyurethane	10-150		87
Coated silica	PMA	150	polymer reinforcement	88
Boehmite				89
Cu <sub>2</sub> S/CdS/ZnS	Polystyrene	2.8-7.1	semiconductor	90

Platy clay mineral reinforced nanocomposites of polyamide, epoxy resins, poly(ethylene oxide), and polystyrene having outstanding mechanical properties have already been commercialized.<sup>82</sup> Spectacular results of reinforcement with cellulose whisker were obtained for styrene butylacrylate copolymer emulsion (6 wt% whisker increased tensile strength by 800-3300% and modulus by 750-16,000%, depending on the method of processing).<sup>84</sup> Because of substantially lower loading with inorganic materials, nanocomposites allow the obtainment of high performance materials at much lower density. Polyamide reinforced with nanoparticles of silicate have improved tensile strength and impact strength and substantially reduced water permeability (Figure 16.25).<sup>86</sup>

Figure 15.42 shows the effect of silica nanoparticles on solvent uptake by the nanocomposite. In addition to much lower solvent uptake, the nanocomposite has increased thermal stability.<sup>91</sup>

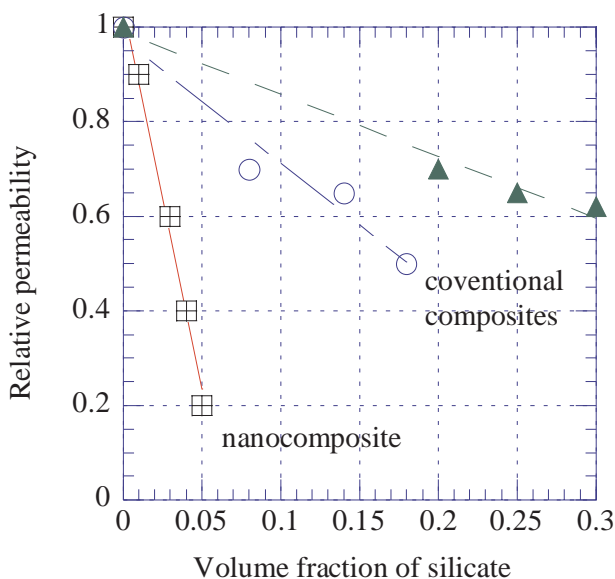


Figure 16.25. Water permeability of nanocomposite and polyamide composite conventionally filled with silicate. [Adapted, by permission, from Giannelis E P, *Adv. Mat.*, **8**, No.1, 1996, 29-35.]

## 16.4 LAMINATES<sup>92-96</sup>

The laminates are not the main focus of this book and thus only a few examples from the current literature are given on filler applications in these products.

Waste incineration requires sophisticated scrubbers to contain corrosive volatiles which are in contact with the scrubber wall at elevated temperatures reaching 220°C.<sup>92</sup> Glass mat reinforced novolac epoxy vinyl ester resins have good performance in this application except that they are subjected to thermal stress due to the temperature difference between surface and wall, and they frequently crack. In order to improve performance, a two layer laminate was produced. The base layer is composed of resin reinforced with glass mat. The resin contains 15-20% graphite filler. The surface layer contains 100 g/m<sup>2</sup> of carbon fiber. The presence of these two fillers helps to distribute heat more evenly throughout the layer of laminate and prevents cracking even under extreme conditions.<sup>92</sup>

The addition of aluminum trihydrate improved fire resistance of glass epoxy laminates but, because of the high loading required, it decreased the mechanical properties of the laminate. Various components of formulation were studied to improve performance. It was found that the curing agent and impact modifier help to improve the mechanical properties of the laminates. Other fillers were also studied in order to understand the impact of filler on properties. It was found that all fillers (glass beads, quartz, calcium carbonate, mica) reduce mechanical properties of laminates, not just aluminum trihydrate.<sup>93</sup> Aluminum trihydrate was found to be one of better performers in this system.

Aluminum particles were used to reinforce glass fiber/epoxy laminates. The fracture toughness was increased but tensile strength and modulus were decreased.<sup>95</sup>

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