

Multipolymer Systems

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The study of structure and the development of structure-property relationships are central issues in materials technology. In the case of organic polymers, structure embraces two distinctly different aspects—molecular structure and supramolecular structure. Molecular structure refers to the macromolecules—their chemical compositions, molecular weights (average molecular weights and distributions of molecular weight), extent of branching or cross-linking, and so on. Supramolecular structure refers to the geometric arrangement of these macromolecules in a specimen. In many cases, the molecular structure of a polymer is established during its synthesis,

A polymer which is employed as a semicrystalline solid can exhibit a variety of different crystalline morphologies, depending on the thermal and mechanical history encountered in its previous mechanical processing (2, 3). For example, linear polyethylene, the simplest prototype of a linear polymer, can exist in any of the following morphologies:

- 1) Spherulitic.
- 2) Drawn fibrillar.
- 3) "Shish kebab."
- 4) Extended-chain crystals.
- 5) Oriented extended-chain crystals.

Spherulitic morphology develops when an unstressed melt is simply cooled. Nucleation of crystallization re-

Summary. Different polymers can be combined to yield a wide variety of composite materials: layered sheets and films, homogeneous and heterogeneous blends, interpenetrating polymer networks, bicomponent fibers, and others. Some properties of a multipolymer material are roughly additive, but synergistic interactions can yield properties and performances superior to those of the individual constituents. Consequently, the use of polymers in combination is a rapidly growing component of polymer materials technology.

whereas the supramolecular structure is established during subsequent mechanical processing into a shaped article. The properties of a polymer depend on both its molecular structure and its supramolecular structure (1).

At high temperatures, a typical linear polymer molecule is in a state of rapid segmental motion, wriggling about from one three-dimensional conformation to another (by means of rotation about covalent bonds within the chain). Under these conditions, the material is a viscoelastic fluid, which can be pumped through channels and formed into desired shapes. Upon cooling, the polymer can solidify by either of two mechanisms: crystallization (ordered packing of chains in a crystal lattice) or vitrification (formation of a glassy amorphous solid). The crystalline melting point, T_M , and the glass transition temperature, T_G , of a given polymeric species are important determinants of its potential applications as a material.

sults in a spherical growing cluster of radially oriented, folded-chain ribbons; mutual impingement of these growing spherulites results in a set of polyhedral grains in the final specimen. Drawing of such a spherulitic structure, below the crystalline melting point, results in a structural reorganization in which chunks of the folded-chain ribbons are oriented into a drawn fibrillar morphology. Crystallization from an oriented melt can result in the shish kebab morphology, consisting of long central fibrils with lateral folded-chain growths. Crystallization under high hydrostatic pressure can lead to extended-chain crystals. The properties of linear polyethylene depend strongly on which of these various morphologies has been developed, as shown in Table 1.

Some polymers are used as glassy amorphous (noncrystalline) solids. Their properties also depend markedly on the supramolecular structure developed during processing—in particular, on the de-

gree of molecular orientation. Polystyrene (PS), a typical glassy noncrystalline polymer, is brittle when unoriented. Uniaxially oriented PS is strong and tough in the direction of orientation, but weak and fragile in the transverse direction. Biaxially oriented PS can be strong and tough in all directions in the plane of orientation (4).

The range of properties obtainable with a given polymer through control of crystalline morphology and molecular orientation can be greatly broadened by the use of different materials in combination: polymers with polymers, polymers with glass or metals, polymers with gases (polymeric foams). The geometric arrangements of the various phases in such composite systems constitute another level of supramolecular structure. Several comprehensive reviews (5, 6) describe the vast scope of polymer-polymer composite materials. Two solid materials can be combined in an infinite number of geometric arrangements: dispersion of particles in a continuous medium, fibers in a continuum, parallel lamellar phases, two interpenetrating continuous phases, and so on. The properties of a particular combination depend on:

- 1) Properties of the individual materials.
- 2) The geometric arrangement.
- 3) The character of the interfaces.

One very important class of polymeric composite materials is that of fiber-reinforced plastics; these are discussed elsewhere in this issue. We will briefly discuss multilayer plastic sheets and films, and polymer blends, and list miscellaneous other examples. First, however, we will examine some basic principles common to all these multipolymer systems.

Miscibility, Immiscibility, and Interfaces

Different low-molecular-weight organic liquids are often miscible in all proportions, but if immiscible, exhibit sharp boundaries between the separate phases. Organic high polymers of differing structures are usually thermodynamically immiscible; even a very small unfavorable heat of mixing per segment adds up to a large value for an entire polymer molecule. Krause (7) lists 17 polymer pairs which appear to be miscible in all proportions at room temperature and 25 pairs which appear to be conditionally miscible, but such miscible systems constitute a small minority among the my-

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Table 1. Young's modulus of linear polyethylene.

Linear PE	Young's modulus (psi)
Transverse to drawn direction	50,000
Spherulitic (isotropic)	100,000
Drawn fibrillar	600,000
"Superdrawn"	9,000,000
Theoretical upper limit	23,000,000

riad possible combinations. Some polymer pairs are miscible at elevated temperatures, but immiscible at room temperature. Other polymer pairs are miscible at room temperature, but immiscible at elevated temperatures.

The phase boundary between two immiscible polymers is more diffuse than boundaries between low-molecular-weight phases; considerable local interpenetration occurs. Although entire polymer chains do not invade the interior of the foreign phase, sections of polymer molecules (loops and tails) can penetrate across the boundary from both sides. This results in a diffuse boundary zone of varying composition which may be 20 or 50 angstroms thick. Two molten polymers which are nearly compatible will have a more diffuse interfacial boundary than a pair of strongly incompatible polymers.

When a two-phase polymer melt is cooled and solidified, the interpenetrating chains may hold the two phases firmly together in the solid state; however, in many cases the phase boundary becomes a site of mechanical weakness—the two solid phases exhibit poor interfacial adhesion. (For example, the act of crystallization may forcibly withdraw some polymer tails which in the molten state penetrated across the boundary, and thus alter the character of the diffuse zone.) A pair of polymers thus may be (i) miscible (a minority of cases), (ii) immiscible, but with strong interfacial adhesion in the solid state, or (iii) immiscible, with poor adhesion.

Two polymers which normally do not adhere well can sometimes be caused to do so by the addition of a third polymer which adheres well to both. Such an agent may be introduced as a discrete "glue layer" between the two non-adhering phases, or may be localized at the interface, with sections of individual molecules penetrating into both phases (8). Figure 1 is a schematic diagram of a block copolymer of A-units and B-units at the interface between the two immiscible phases poly-A and poly-B. Such an additive can tie together two immiscible polymers which would otherwise exhibit poor interfacial adhesion.

These features of compatibility or incompatibility, interfacial adhesion, and "compatibilizing" additives are critical in all types of multipolymer systems—layered films, polymer blends, and fiber-reinforced polymers.

Multilayer Plastic Sheets and Films

The use of polymers in layered combination is quite old. The utility which could be gained by combining layers with different desirable properties often justified the expense of multiple operations—laminating films together, applying coatings, and so on. In recent years, an inexpensive method of producing such laminar structures has led to a rapid growth in the number and quantity of such products. Two or more molten polymers are combined as fluid layers within a die, and the layered product is produced directly in one step. Today, many layered plastic sheets and films are manufactured by melt coextrusion (9). Figure 2 is a schematic diagram of one method of producing coextruded laminar products. Individual streams of molten polymers are introduced through feed ports and joined together in a parallel array. This multilayer fluid passes through a transition zone in which the layers are extended laterally and thinned down, while remaining parallel. Finally, the multilayer fluid exits through a wide, shallow die opening and is cooled to yield the solidified layered product. Films containing hundreds of layers can be produced in this manner; most commercial coextruded products contain from two to seven layers. Figure 3 illustrates a few typical examples. Often a desired laminar structure contains adjacent layers which exhibit poor interlayer adhesion; this compels the introduction of a thin glue layer of a polymer which will adhere well to both (9).

The properties of a multilayer polymer sheet depend on:

- 1) The properties of the individual polymers.
- 2) The layer geometry.
- 3) The character of the interfaces.

Some sheet properties turn out to be derived from those of the individual layers by simple addition or averaging. In other cases, synergistic interactions result in sheet behavior which is significantly different from the sum of its parts. Finally, some multilayer films exhibit characteristics which are unique.

Barrier to diffusion—an additive property. An important group of applications for layered polymer products is in the packaging of food, medical products,

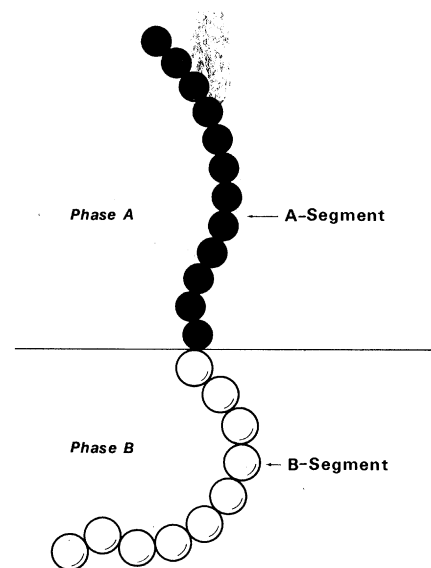


Fig. 1. An A-B block copolymer molecule located at the interface between two immiscible polymers, poly-A and poly-B. High-molecular-weight copolymers would have many more units than are shown here.

chemicals, and so on. Many of these applications demand low permeability to oxygen, water vapor, or other migrating species. Normally, the diffusion barrier provided by a multilayer sheet is the simple sum of the barrier values of the individual layers ("resistances in series") (10). Polymers differ greatly in their permeabilities to small molecules; for example, the permeability of low-density polyethylene to O_2 is more than 1000 times that of Saran. Thus, a relatively thin barrier layer of one polymer can be combined with other layers chosen for mechanical toughness, heat sealability, or other required properties, to yield a superior packaging film or a sheet which can be formed into containers.

Mechanical properties. Some mechanical properties of multilayer sheets are similarly additive. However, it is often observed that a thin layer in a laminate behaves much differently from a free film of the same material. Particularly striking effects can be observed in laminar composites containing a hard component and a soft component, or a brittle component and a tough component. Sword makers of early times hammered down alternate layers of hard and soft steel, obtaining blades that would take a fine cutting edge and yet were strong and tough (11). Similar effects can be observed with coextruded multilayer polymer systems (10).

Consider a laminar composite containing a layer of high-modulus, low-elongation material flanked by layers of more extensible materials. When the composite is tested to failure in tension, the

adhering high-elongation layers may act to prevent transverse crack propagation in the hard layer. With crack propagation so blocked, the hard layer may be able to reach its ductile yield stress, and the entire composite can stretch in a ductile manner to high elongation. This toughening effect has been termed mutual interlayer reinforcement (10). Interlayer interaction can sometimes have the opposite effect; a normally tough polymer may act in a brittle manner in a laminar composite. In this case the high-elongation material is not able to block crack propagation in the brittle layer; a crack forms in the brittle layer, and continues into and through the tough layer, causing a localized failure at low overall elongation. For example, a skin of general-purpose PS on a core of high-impact PS can force the entire composite to undergo brittle failure on bending. This behavior has been called mutual interlayer destruction (12). Such interlayer interactions, whether of a beneficial or a deleterious nature, require some degree of adhesion at the interfaces. However, the thinner the layers, the lower will be the degree of adhesion required for one layer to alter the response of its neighbor.

The mechanical properties of each layer in a laminar composite depend on the molecular orientation present. As with homogeneous sheets, uniaxial orientation can increase tensile strength in one direction while reducing it in the other direction. Biaxial orientation can provide desirable mechanical properties in all directions in the plane. In a multilayer polymer film, an appropriate amount of biaxial orientation can optimize the mechanical properties of the individual layers, and thereby the likelihood and extent of interlayer reinforcement. For example, biaxially oriented 125-layer films of polypropylene and PS have been reported to exhibit high tensile strengths and high ultimate elongations over a wide composition range (10).

Optical properties. Finally, multilayer films made of alternating layers of two transparent polymers with differing refractive indices can exhibit vivid optical effects. In nature, the iridescent colors of many butterflies, beetles, birds, and fish result from selective reflection from layered microstructures (13). Similar effects are observed with coextruded multilayer polymer films (14, 15). Figure 4 is a schematic drawing of a 125-layer film in which the odd layers have a refractive index of 1.6 and the even layers a refractive index of 1.5. When a beam of light of wavelength λ shines on the film, partial reflection occurs at each of the many in-

terfaces; the reflections at the interfaces of increasing refractive index suffer a phase reversal. Since the layers differ by only 0.1 in refractive index, the individual reflections are weak. However, if reflections from the different interfaces all leave the film in phase with each other, the constructive interference yields a high-intensity reflection. The wavelength of the first-order reflection (for normal incidence) is given by

$$\lambda_1 = 2(n_{\text{odd}}d_{\text{odd}} + n_{\text{even}}d_{\text{even}})$$

where n and d are refractive index and thickness. For example, if the thicknesses of the odd and even layers are set at 700 and 746.5 Å, respectively

$$n_{\text{odd}}d_{\text{odd}} = 1.6 \times 700 = 1120$$

$$n_{\text{even}}d_{\text{even}} = 1.5 \times 746.5 = 1120$$

$$\lambda_1 = 2(1120 + 1120) = 4480 \text{ Å}$$

In addition to the first-order reflection, λ_1 , higher-order reflections occur at wavelengths λ_{II} , λ_{III} , . . . , which are 1/2,

1/3, 1/4 . . . of the λ_1 value. The relative intensities of these higher order reflections depend on the ratio of optical thicknesses of the two kinds of layer. For example, if the odd and even layers have equal optical thickness, the second-order and fourth-order reflections are suppressed. On the other hand, if $n_{\text{odd}}d_{\text{odd}} = 2n_{\text{even}}d_{\text{even}}$, the third-order reflection is suppressed.

In the illustration above, where the layer thicknesses are uniform through the film, the reflection at 4480 Å would involve only a narrow band of wavelength. The reflected color would be "pure," but "pale." If the layer thicknesses are appropriately varied through the film, a broader band of wavelength will be reflected. Theoretically, the most vivid color impression, called a C-color, corresponds to strong reflection extending over a spectral region bounded by two complementary wavelengths; this provides the optimum compromise between intensity and color purity (16).

Fig. 2. Schematic diagram of the feed-block method of coextruding multilayer polymer sheets and films.

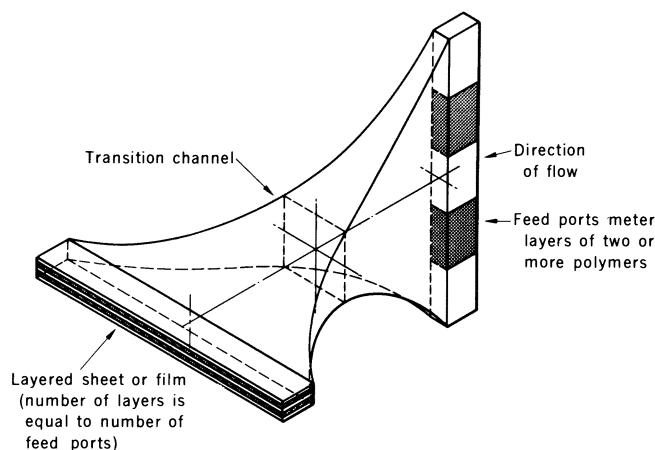
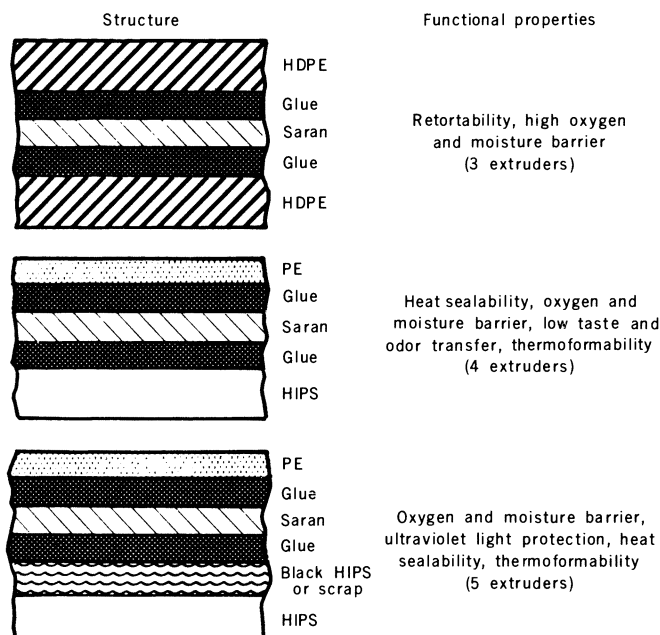


Fig. 3. Schematic diagram of some multilayer plastic sheets with functional properties developed by the combinations of layers.



with PVC and unchlorinated sections miscible with PE. Finally, some immiscible polymer pairs exhibit strong interfacial adhesion without the need for any compatibilizer.

Interpenetrating polymer networks (IPN's). Manson and Sperling (5, chap. 8) have described a broad class of polymer structures involving two intimately interlocked polymer networks. One way to produce such a structure is to start with a lightly cross-linked polymer, A, swell it with a second monomer, B (plus cross-linker), and polymerize B. A second polymer network (B) forms within the space enveloped by the first. The two polymer networks are distinct, but physically interpenetrating. Another way to prepare an IPN structure is to simultaneously polymerize two mixed monomers with their cross-linkers, by separate non-interfering polymerization mechanisms (for example, styrene plus divinylbenzene polymerized by a free radical mechanism, in the presence of a polyurethane network being formed by polycondensation). Whether formed simultaneously or sequentially, IPN's commonly undergo restricted phase separation into microdomains rich in the respective polymer species. An IPN of polyethylacrylate (PEA) and polymethylmethacrylate (PMMA), which are nearly miscible polymers, has phase domains smaller than 100 Å. In the case of PEA-PS, a more immiscible pair, a cellular structure about 1000 Å in size develops. The properties of an IPN depend on the properties of the individual polymers, the phase morphology, and interactions between the phases (5, chap. 8). Some IPN properties are simple averages of the individual polymer properties; other properties may be synergistic. Practical exploitation of this broad class of materials can be anticipated.

High-impact polystyrene (HIPS). Polystyrene is a useful and important thermoplastic material which is rather brittle. This glassy polymer can be toughened by appropriate molecular orientation, or by the introduction of dispersed rubber particles. HIPS is produced by dissolving a rubber in styrene monomer, which is then polymerized. Since PS and rubber are immiscible, phase separation accompanies polymerization. Initially, the PS phase is dispersed in a continuous rubber phase (both highly swollen with styrene monomer). Mechanical agitation causes a phase inversion to occur, yielding a continuous PS phase with dispersed rubber particles. Further formation of PS occurs in both phases, the final product having a continuous PS phase and dispersed rubber particles, within which PS inclusions

are embedded—an A-in-B-in-A dispersion. The properties of this dispersion, produced by combined chemical and mechanical means, are different from those of a simple melt blend of the same amount of rubber with PS. HIPS is much tougher than PS, but less transparent.

Multicomponent Textile Fibers

Textile products containing more than one polymer are now common. Different polymers can be used in combination at various levels. A garment might be made from sections of nylon cloth and polyester cloth. Nylon yarn could be interwoven with polyester yarn to yield a composite fabric. Nylon fibers could be spun together with polyester fibers to yield a composite yarn. Finally, molten nylon and polyester polymers can be coextruded to yield composite fibers. At some point in this series, it becomes appropriate to regard the composite as a new material, with its own distinctive material properties.

Although the textile industry combines polymers at the level of garment, fabric, yarn, and fiber, this discussion will be limited to the coextrusion of two

different polymers to form bicomponent or biconstituent fibers. The term bicomponent is applied to skin-core fibers and side-by-side two-component fibers, prepared by supplying two separate feed streams to each die opening. When two molten polymers are blended to disperse the minor component as droplets, and then melt-spun and drawn to produce a dispersion of parallel, oriented fibrils within each fiber, the term biconstituent fiber is used. Bicomponent fiber manufacture has many parallels to the coextrusion of multilayer sheets and films (see above), and biconstituent fibers represent a special case of polymer blend technology.

Figure 5 illustrates the wide range of phase arrangements within multicomponent textile fibers which can be developed by such coextrusion processes. Some of these represent commercial products; others are taken from patents. Still another possible phase morphology is a bicontinuous structure similar to the interpenetrating polymer networks discussed earlier; Paul (22) indicates that the mechanical interlocking of the two phases in such a fiber reduces the need for adhesion between the phases. Finally, the fiber composition or morphology can be deliberately varied along the length in order to develop desired properties.

Some properties of bicomponent and biconstituent fibers are essentially additive with respect to the individual polymer constituents, but some properties are synergistic or even unique. One important practical phenomenon often observed with bicomponent fibers is self-crimping. If one side of a bilateral fiber tends to shrink more on heating than the other side, the fiber can be made to develop a spontaneous helical crimp. Fiber crimp is important in the spinning of staple yards and in the mechanical behavior of the eventual fabrics. (High bulk and high stretchability are examples of fabric properties which can be developed by use of self-crimping bicomponent fibers.)

Other applications of multipolymer fibers include antistatic fibers, nylon tire-cord with reduced "flat spotting," flame retardance, improved dyeability, and bondable fibers for nonwoven fabrics.

Bicomponent fibers with low interfacial adhesion can be fibrillated (split apart) to yield blends of ultrafine fibrils. In this case, poor adhesion is an exploitable advantage rather than a deficiency. Rasmussen (23) developed a process for producing bicomponent fibers from multilayer film. Three polymers are coextruded into the layer sequence AB-

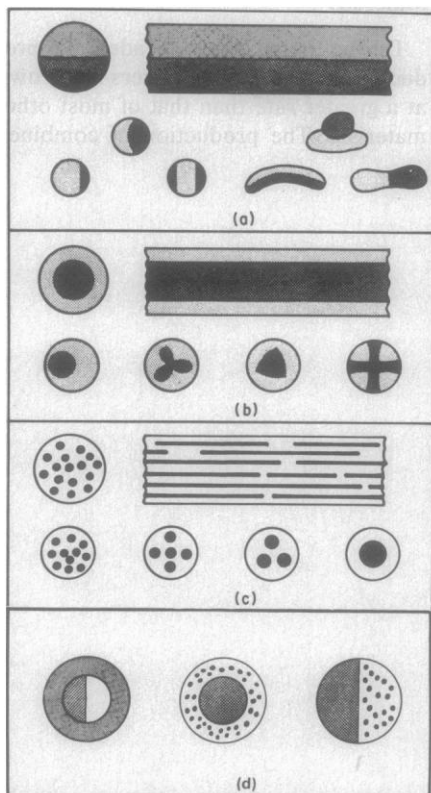


Fig. 5. Possible bicomponent and biconstituent fiber structures: (a) side-by-side, (b) sheath-core, (c) dispersed fibrillar, and (d) combinations. [After Paul (6, vol. 2, pp. 171 and 173)]

CABC . . . , where B adheres to A and C but the A-C interfaces can delaminate. The multilayer melt stream is extruded through orifices, drawn into thin ribbons, and mechanically delaminated to form very thin bicomponent fibers (components A and C held together by the adhesive B).

Expanded Polymers (Foams)

Still another class of two-phase polymer structures, which further broadens the range of useful material properties, is the versatile family of foamed polymers. Nature produces and man utilizes many lightweight polymeric materials which contain large amounts of distributed void-space (cork, balsa, sponges). These natural materials have been joined by a wide variety of synthetic polymers in expanded or foam form. A few examples are foamed rubbers, expanded PS, and rigid and flexible polyurethane foams. These expanded polymers find wide and growing applications in thermal insulation, cushioning (furniture, automobiles), packaging, and construction.

Expanded polymers can be rigid or flexible, open-cell or closed-cell, crystalline or amorphous, thermoplastic or thermosetting, high-density or low-density. The range of possible structures (and properties) is very great. The compressive softness of an open-cell elastomeric foam is an obvious characteristic. Less obvious is the fact that rigid foams can answer structural needs in appli-

cations requiring high rigidity. The bending rigidity of a plate or shell increases with the cube of its thickness; consequently, a plate or shell composed of a rigid plastic foam has a much greater bending stiffness than a (thinner) plate made from the same weight of unfoamed polymer (even though the foam modulus is low).

This capacity for lightweight rigidity can be augmented by preparing sandwich structures with high-modulus skins and rigid foam cores (a structural principle long utilized by nature in the load-bearing bones of birds). Plastic foam cores can be combined with sheet-metal skins, or plywood skins, to yield such structural panels. Alternatively, a foaming polymer can be molded in such fashion as to directly produce a finished shaped article with a foamed core and a dense, unfoamed skin; such systems are referred to as structural foams. The properties of an expanded polymer depend on the properties of the polymer (or polymers) and the foam morphology. The versatility of polymer foams can be further expanded by the incorporation of additional phases, such as reinforcing fillers.

Industrial Growth of Multipolymer Materials

During the past few decades, the production of synthetic polymers has grown at a greater rate than that of most other materials. The production of combined

polymeric materials is growing faster yet—coextruded multilayer sheets and films, polymer blends, bicomponent fibers, foams (including structural foams), and fiber-reinforced plastics. This rapid industrial growth is largely due to the enhanced utility which can be achieved with polymers by varying and controlling the supramolecular structures as well as the molecular structures of these materials.

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