POLYMER BLENDS

1. Introduction

Mixing of two or more different polymers together makes possible to achieve various property combinations of the final material, mostly in a more cost-effective way than in the case of synthesis of new polymers. Therefore, great attention has been paid to the investigation of these systems as well as to the development of specific materials. Recently, the problem of polymer blends has become important also for recycling industrial and/or municipal plastics scrap. Considerable information has been collected during more than three decades and summarized in many monographs (see *General References*).

Basic problems associated with the equilibrium and interfacial behavior of polymers compatibility of immiscible components and phase structure development including the methods of its investigation, are described. Special attention is paid to mechanical properties of heterogeneous blends and their prediction. Commercially important types of polymer blends as well as the recycling of commingled plastic waste are briefly discussed.

2. Equilibrium Phase Behavior

Mixing of two amorphous polymers can produce either a homogeneous mixture at the molecular level or a heterogeneous phase-separated blend. Demixing of polymer chains produces two totally separated phases, and hence, leads to macrophase separation in polymer blends. Some specific types of organized structures may be formed in block copolymers due to microphase separation of block chains within one block copolymer molecule.

Two terms are usually used in literature, miscible blend and compatible blend. The terminology recommended by Utracki (1) is used in this article. A *miscible polymer blend* means a blend of two or more amorphous polymers homogeneous down to the molecular level and fulfilling the thermodynamic conditions for a miscible multicomponent system. An *immiscible polymer blend* is a blend that does not comply with the thermodynamic conditions of phase stability. The term *compatible polymer blend* indicates a commercially attractive polymer mixture, which is visibly homogeneous, frequently with improved physical properties compared with the constituent polymers.

Equilibrium phase behavior of polymer blends complies with the general thermodynamic rules (2–6)

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} < 0 \tag{1}$$

and

$$\mu_i' = \mu_i'' \qquad i = 1, 2, \ldots, n \tag{2}$$

where ΔG_{mix}, ΔH_{mix}, and ΔS_{mix} are the Gibbs energy, enthalpy, and entropy of mixing of a system consisting of i components, respectively; μ'_i and μ''_i are the chemical potentials of the component i in the phase′ and phase″. The condition given in equation 1 is necessary, but it is not sufficient. Equation 2 must be also fulfilled.

Generally, for a compressible polymer blend the following requirement must be satisfied (5–7)

$$\left(\frac{\partial^2 \Delta G_{\text{mix}}}{\partial v_i^2}\right)_{T,P} = \left(\frac{\partial^2 \Delta G_{\text{mix}}}{\partial v_i^2}\right)_V + \left(\frac{\partial V}{\partial P}\right)_{T,v_i} \left(\frac{\partial^2 \Delta G_{\text{mix}}}{\partial v_i \partial V}\right) > 0 \tag{3}$$

where v_i is the volume fraction of component i; V is the molar volume of blend; P is pressure; and T is the temperature of the system. For incompressible system with $\Delta V_{\text{mix}} = 0$, the Flory-Huggins equation for ΔG_{mix} can be used (4). Thus, phase stability is obtained

$$\frac{1}{N_1 v_i} + \frac{1}{N_2 v_2} - 2\chi_{12} \geq 0 \tag{4}$$

where N_1, N_2 are the numbers of segments of polymer 1 or 2, and χ_{12} is the interaction parameter between polymers 1 and 2. The entropy contribution (the first and second terms on the left-hand side of equation 4 supporting miscibility of polymers is practically zero (N_1, $N_2 \gg 1$). In this case, the miscibility is controlled by the enthalpy of mixing (interaction parameter χ_{12}). For nonpolar polymers, without strong interactions, the temperature dependence of χ_{12} (Fig. 1, curve 1) is given as

$$\chi_{12} = A + B/T \tag{5}$$

where A and B are positive constants characterizing enthalpy and entropy of the interaction parameter χ_{12}, respectively. Its positive value indicates a very poor miscibility of high molecular weight nonpolar polymers.

Relations considering the compressibility of polymer blends are based on the equations-of-state theories (5,6,8–16). These relations include contributions

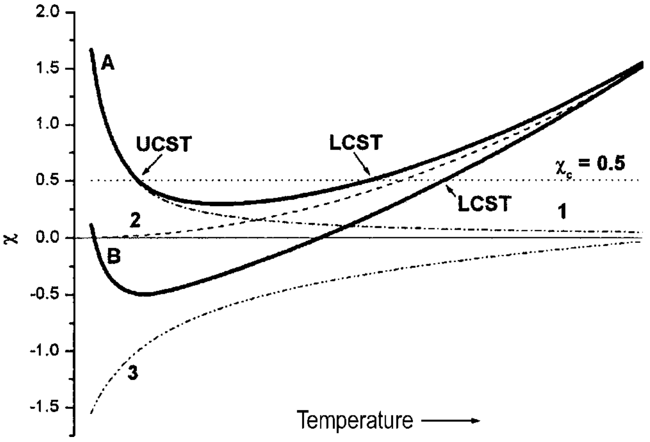


Fig. 1. Temperature dependence of interaction parameters resulting from different types of interactions in a polymer blend. (1, dispersive interactions, 2, free-volume interactions, 3, specific interactions, A sum of 1+2, B sum of 1+2+3).

to the entropy and enthalpy of mixing resulting from volume changes during mixing. The temperature dependence of free-volume interaction is schematically presented as curve 2 in Fig. 1. Its value plays a decisive role in determining phase behavior of a polymer blend at a high temperature range.

From the equation 4, it follows that the negative value of parameter χ_{12} is necessary to obtain a stable homogeneous polymer blend. The negative value of χ_{12} is characteristic of systems with specific interactions such as dipole–dipole or hydrogen bond interactions (1,5,6,17). A schematic representation of the temperature dependence of a specific interaction parameter (13), is given in Fig. 1, curve 3.

The critical value of the interaction parameter χ_c for "symmetric" polymer blends of polymers 1 and 2 ($N_1 = N_2 = N$, N- number of segments in polymer chain) is $\chi_c = 2/N$. When the χ_{12} value crosses the critical value, a polymer blend separates into two macrophases. The character of the temperature dependence of χ_{12} determines the shape of the phase diagram (Fig. 1). Figure 2 is a schematic binodal and spinodal curves corresponding to the different types of interaction parameters presented in Fig. 1. Binodal curves (Fig. 2, curves 1–4), defining the two-phase region, are calculated from equation 2 (2,4–6,18). A spinodal curve is obtained by solving equation 4. The spinodal curve defines the region of absolute instability of the polymer blend. The point common to the binodal and spinodal curves is the critical point. The position of the critical point of a blend of monodisperse polymers coincides with the maximum (UCST) or minimum (LCST) of a binodal curve (18). The upper critical solution temperature (UCST) lies at the maximum of binodal curve. The lower critical solution temperature (LCST) lies at the minimum of binodal curve (Fig. 2). If only dispersive interactions among polymer molecules are effective in blend (Fig. 1, curve 1) partial miscibility can be expected at low temperatures. Above the UCST, the polymer blend is homogeneous (Fig. 2 curve 1) (4–6). Values of interaction parameters of nonpolar polymers can be found in the

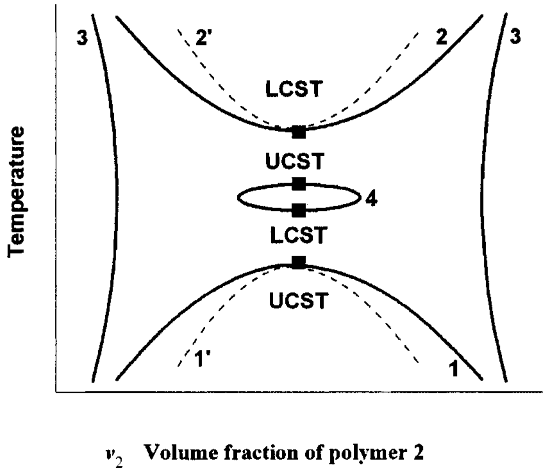


Fig. 2. Possible types of phase diagrams corresponding to interactions in Fig. 1 (—— binodal curves, ------ spinodal curves. UCST = upper critical solution temperature, LCST = lower critical solution temperature)

literature (1,5,6) or estimated from the solubility parameters δ_1, δ_2, of the neat components

$$\chi \approx (\delta_1 - \delta_2)^2 \tag{6}$$

The χ parameter of disperse interactions is always positive and miscibility is driven only by combinatorial entropy of mixing. In general, nonpolar polymers are rarely miscible with each other. Much data relevant to interaction energies obtained by different techniques can be found in the literature (5,6,19,20).

The area below the spinodal curve is the region of absolute instability of a polymer blend. The phase separation in this region is controlled by a spinodal mechanism. The region between the spinodal and binodal curves is called the metastable region. The phase separation in this region is controlled by nucleation mechanism.

Phase structure at an initial stage of phase decomposition depends on the type of its mechanism. Characteristic of the spinodal decomposition in an absolutely unstable region is phase separation in the whole volume of the blend. The resulting structure is very fine, but gradually gets coarse (5,21) and the final stage of separation is a complete macrophase separation. If the phase separation takes place in the metastable region, the decomposition of the blend depends on the formation of a nucleus of a new phase. The resulting structure at the initial stage is grainy. The critical sizes of existing nuclei increase by Ostwald ripening mechanism (16). Small grains dissolve and large grains grow due to the dependence of the concentration gradient of dissolved molecules of nucleating component. The dissolved molecules are dependent on radius of grains. At the final stage, when the separation is finished, a full phase-separated structure is again obtained (5).

In an unstable region, fluctuations increase. The fluctuations can be considered as a set of sinusoidal waves with a constant length (6,16). The amplitude of the fluctuations in the initial stage of the phase separation increases with the time as described in Ref. 6. The phase structure of the system is cocontinuous for a broad range of the blend compositions. At the end of the process, separated phases are identical with the blend components. Theories have been developed that describe the various stages of spinodal decomposition (using various approximations), (16). For the most part, scattering methods have been used for experimental studies of the phase-structure decomposition in polymer blends. The initial, intermediate, and late stages of the phase-stucture separation differed depending on the domain size of individual phases with time, were recognized. The individual stages of the phase-structure development are described by the different dependences of the phase domains size with time. The development of spatial concentration fluctuation is generally described by the Ginsburg-Landau equation. It considers chemical potential as a function of order parameter, contribution of the random forces, and the hydrodynamic interaction between polymer molecules (16). Similar equations describe also polymer dissoultion if, due to a change in thermodynamics parameters, an immiscible blend becomes a miscible one. The phase separation is affected by the presence of a copolymer and by a shear flow (16). A detailed description of the kinetics of the phase decomposition in polymer blends can be found in Ref. 16.

If there is system with free-volume or specific interactions, an increase in temperature causes phase separation at LCST. In real systems, where several types of interactions are effective, the phase behavior with two regions of partial miscibility of components with UCST and LCST (Fig. 2, binodals 1 and 2) or hourglass-shaped binodal and spinodal curves (Fig. 2, binodal 3) can be expected (5,6,9,13–16). In some cases a closed loop of immiscibility with LCST and UCST (Fig. 2, binodal 4) or a closed loop and region of partial immiscibility at high temperatures with LCST (Fig. 2, binodals 2 and 4) are observed. This pattern of phase behavior is caused by the diminishing intensity of specific interactions with increasing temperature.

Whether polymers are miscible or not it depends on a delicate balance of interactions among all components in system (6). Any favorable gain in the energy of mixing is accompanied with an unfavorable noncombinatorial entropy effect (22,23).

The effective value of interaction parameter χ_{eff} of a multicomponent polymer blend is controlled by its composition. Blends containing statistical copolymers of A and B monomers can be used as examples. Using the mean-field theory leads to the following relation for χ_{eff}

$$\chi_{\mathrm{eff}} = \sum_{\mathrm{i}} \sum_{\mathrm{j>i}} \chi_{\mathrm{ij}} \left(v_{\mathrm{i}}^{A} - v_{\mathrm{i}}^{B} \right) \ \left(v_{\mathrm{i}}^{B} - v_{\mathrm{i}}^{A} \right) \tag{7}$$

where χ_{ij} is the interaction parameter between segments i and j. For the same type of segments, its value is 0. It follows from equation 7 that at a proper composition of copolymers, the value of χ_{ij} can be negative and the resulting blend of these copolymers is homogeneous.

The former discussion deals with liquid–liquid phase behavior; however, sometimes one or both components of the blend can crystallize. For a polymer pair that is miscible in the melt, cooling well below the melting point of pure crystallizable component leads to form a pure crystalline phase of that component. Far below the melting point, the free energy of crystallization is considerably larger than that of mixing. Because polymers never become 100% crystalline, the pure crystals coexist with a mixed amorphous phase containing the material that did not crystallize (6,7).

The morphology of heterogeneous polymer blends is controlled by interfacial tension. The interfacial tension σ is intrinsically positive and can be defined as the change in the Gibbs energy when the interfacial area A is reversibly increased at constant temperature and pressure at closed system (24).

$$\sigma = \left(\frac{\partial G}{\partial A}\right)_{T,P} \tag{8}$$

In a multicomponent system the tendency to minimalize Gibbs energy leads to migration of minor component to the interface. The resulting concentration increase of this component on the interface (compared to its concentration in the bulk) (24) decreases the interfacial tension as follows

$$\frac{\partial \sigma}{\partial \, \mathrm{In}\, c_2} = -RT(\Delta\, N_2/VN_1) \tag{9}$$

where c_2 is the molar concentration of the component 2, ΔN_2 is the excess number of molecules of the component 2 on the interface, N_1 is the number of molecules of component 1 and V is the volume of the system. Therefore low energy additives can greatly reduce the interfacial tension between polymers and hence are expected to increase the degree of dispersion in blends. Block and graft copolymers are the most effective interfacial agents. They show considerable surface activity on the low energy components. Their emulsifying property depends on their structure.

3. Compatibilization

The blends of immiscible polymers obtained by simple mixing show a strong separation tendency of the components leading to a coarse structure and low interfacial adhesion. The final material then exhibits poor mechanical properties. On the other hand, the immiscibility or limited miscibility of polymers enables formation of a wide scale of various structures. Some of them, if stabilized, can impart excellent end-use properties to the final material. To obtain such a stabilized structure, it is necessary to ensure a proper phase dispersion by decreasing interfacial tension, to suppress phase separation, and to improve adhesion. This can be achieved by modification of the interface, consisting in the formation of bonds (physical or chemical) between the polymers. This procedure is known as the compatibilization and the active component creating the bonding as the compatibilizer (1,6,7). Two general methods are used for compatibilization of immiscible polymers: incorporation of suitable block or graft copolymers; or reactive compatibilization.

3.1. Incorporation of Copolymers (Nonreactive Compatibilization). Block or graft copolymers whose segments are miscible with the respective polymer components show a tendency to localize at the interface between immiscible blend phases. They anchor their segments in the relevant polymer, reduce interfacial tension, and stabilize dispersion against coalescence (24–52). Random copolymers, sometimes also used as compatibilizers, reduce interfacial tension but their ability to stabilize the phase structure is limited (53). Finer morphology and higher adhesion lead to improved mechanical properties. The morphology of the resulting two-phase (multiphase) material and, consequently, its properties depend on a number of factors such as copolymer architecture (type, number, and molecular parameters of segments), blend composition, blending conditions etc (25,38,39). Creton and co-workers (54) have reviewed the molecular criteria for the copolymers linking two immiscible homopolymers that must be fulfilled to achieve good stress-transfer ability of the interface. A schematic of the conformation of different block, graft, or random copolymers at the interface is shown in Fig. 3.

Besides copolymers synthesized especially for compatibilization of immiscible polymers, commercial products (used usually as impact modifiers) are utilized as compatibilizers in research as well as in practice. Typical examples are styrene–butadiene block copolymers and their styrene–hydrogenated butadiene analogues used for compatibilization of styrene polymers with polyolefins (49) or ethylene–propylene copolymers for compatibilization of various polyolefins (50).

The mechanical properties sensitive to stress transfer are usually considered as the criteria of the compatibilization efficiency because they indirectly characterize interface adhesion (1,7,45). Also morphological characteristics such as particle size of the dispersed phase, structure homogeneity, character

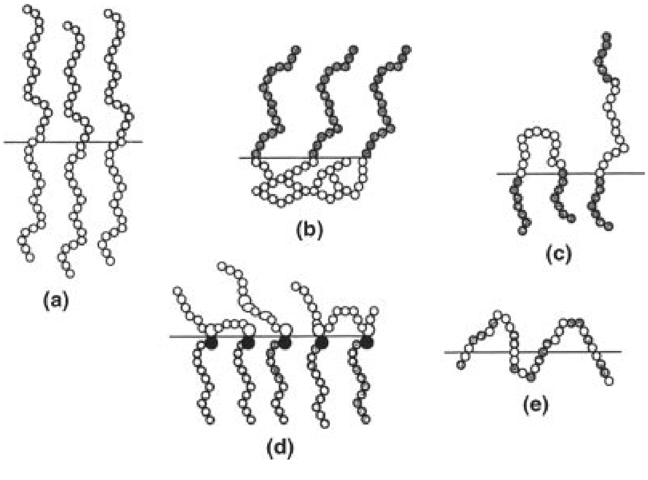


Fig. 3. Possible localization of A-B copolymer at the A–B interface. Schematic of connecting chains at an interface. (**a**) Diblock copolymers, (**b**) end-grafted chains, (**c**) triblock copolymers, (**d**) multiply grafted chain, and (**e**) random copolymer (Reproduced with permission from Ref. 54).

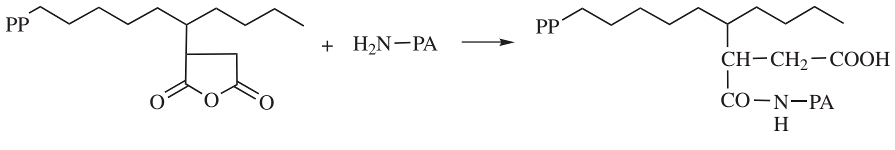
of interfacial layer, existence of micelles or mesophases is an indicator of the compatibilization efficiency (25,29,40–44).

This process, however, has two practical limitations. Blending of an immiscible polymer pair requires a specific block or graft copolymer. Consequently, a specific synthetic procedure is necessary to obtain the desired copolymer. This can be costly and sometimes there is no feasible technology at manufactureŕs disposal. Moreover, the amount of the copolymer to be added is often significantly higher than that for saturation of the interface. A part of the copolymer may be trapped during blending in the bulk phase and never reaches the interface. This fact can negatively affect the blend morphology and may lead to higher compatibilizer consumption.

For more than three decades, much data on the nonreactive compatibilization has been obtained which is successfully applied in the development of new multiphase materials. Moreover, the proved efficiency of block or graft copolymers in the controlling of the phase structure development has led to new, more effective approaches to produce these copolymers directly during the blending. This process is known as the reactive compatibilization.

3.2. Reactive Compatibilization. Reactive compatibilization is the process that allows generating graft or block copolymers acting as compatibilizers *in situ* during melt blending (46,55). These copolymers are formed by reactions at the interfaces between suitably functionalized polymers, and so they link the immiscible phases by covalent or ionic bonds. In this process, the copolymers are formed directly at the interfaces where they act like preformed copolymers, ie, they reduce the size of the dispersed phase and improve adhesion. For this reason, the problem with transport of the compatibilizer to interface is not relevant and so the structure control is easier than in the case of adding of preformed copolymers. In order to achieve efficient compatibilization of polymer blends, the reactions between the functional groups should be selective and fast, and the mixing conditions should minimize the limitation of mass transfer in the course of the reaction.

There are several cases of reactive compatibilization. If the mixed polymers contain reactive groups, the reaction is straightforward. The polymers without reactive groups have to be functionalized or a miscible polymer containing proper reactive groups is added to the respective component. Therefore reactive groups such as anhydride, hydroxy, amine, carboxy are incorporated to one or both of the polymers to be compatibilized. Maleic anhydride-grafted polymers such as polypropylene (PP), polyethylene (PE), ethylene−propylene rubber (EPR), ethylene−propylene−diene rubber (EPDM), styrene−ethylene/butylene−styrene (SEBS) or acrylonitrile−butadiene−styrene (ABS) (46,55), which can react with polymers containing amino group, serve as examples:



Reactive compatibilization of polymers through copolymer formation is possible with the help of low molecular weight compounds (56), eg, by combination of a peroxide with an oligomer coagent that is used for preparation of PE/PP blends (57) or bis(maleic imide) used for preparation of PE/PBT (58). Special cases of reactive compatibilization can be considered radical-initiated reactions of monomers, which form beside homopolymers, grafts on the chains of dissolved polymers. This process is used for manufacture of such important polymers as high impact polystyrene (HIPS) or ABS (59).

4. Preparation and Phase-Structure Development

4.1. Methods of Blend Preparation. Most polymer pairs are immiscible and, therefore, their blends are not formed spontaneously. Moreover, the phase structure of polymer blends is not equilibrium and depends on the process of their preparation. Five different methods are used for the preparation of polymer blends (60,61): melt mixing; solution blending; latex mixing; partial block or graft copolymerization; and preparation of interpenetrating polymer networks. Due to high viscosity of polymer melts, any of these methods is needed for the size reduction of the components (to the order of μm) even for miscible blends.

Melt mixing is the most widespread method of polymer blends preparation in practice. The blend components are mixed in molten state in extruders or batch mixers. Advantages of the method consist in well-defined components and universality of mixing devices; the same extruders or batch mixers can be used for a wide range of polymer blends. Disadvantages of the method are high consumption of energy and the possibility of unfavorable chemical changes of the blend components.

In several past years, novel solid-state processing methods, such as shear pulverization or cryogenic mechanical alloying, have been developed to provide efficient mixing of polymer blends (62,63). The polymers are desintegrated in pulverizers at cryogenic temperatures and nanoscale blend morphologies are achieved. Since the blends are prepared as solid powders, they must be consequently processed in the melt for a concrete manufacture. The mechanochemistry of this process makes it possible to obtain block or graft copolymers acting as compatibilizers. Despite to advantages, this procedure has not been used so far in industrial practice because it consumes large amounts of energy.

Solution blending is frequently used for preparation of polymer blends on a laboratory scale. The blend components are dissolved in a common solvent and intensively stirred. The blend is separated by precipitation or evaporation of the solvent. The phase structure formed in the process is a function of blend composition, interaction parameters of the blend components, type of the solvent, and history of its separation. Advantages of the process are rapid mixing of the system without large energy consumption and avoidance of unfavorable chemical reactions. On the other hand, the method is limited by the necessity to find a common solvent for the blend components, and in particular, to remove huge amounts of organic, frequently toxic, solvent. Therefore, in industry, the method is used only for preparation of thin membranes, surface layers, and paints.

A blend with heterogeneities of 10 μm order can be prepared by mixing of latexes without using organic solvents and consumption of large amounts of energy. Most energy is needed for removing water and eventually for achieving a finer dispersion by melt mixing. The whole energetic balance of the process is usually better than that for melt mixing. The need to have all components in the form of latex limits the use of this process. Because this is not the case with most synthetic polymers, the use of this process in industrial practice is limited.

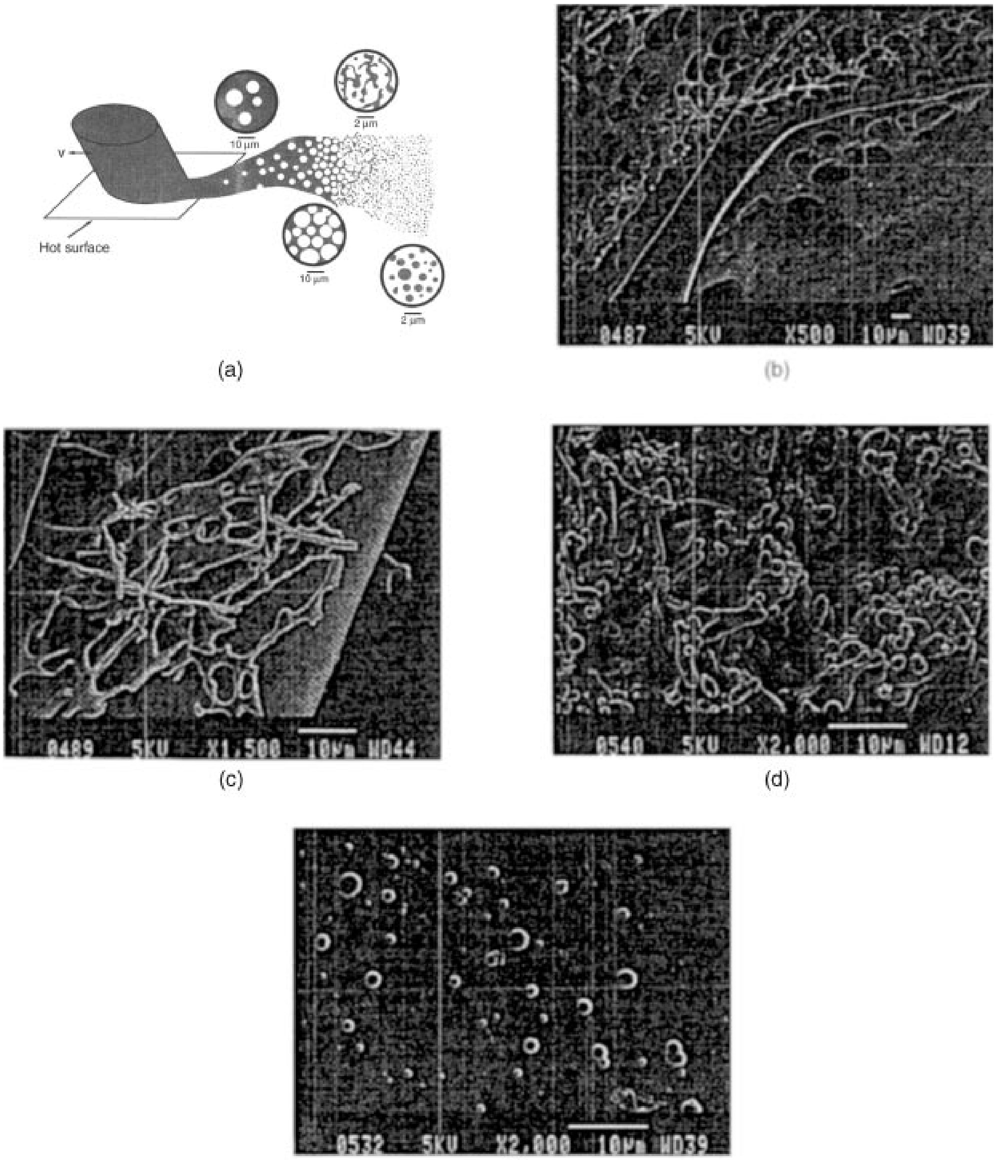
In partial block or graft copolymerization, homopolymers are mostly synthesized, but the amount of a copolymer sufficient for obtaining good adhesion between immiscible phases is formed (59). In most cases, materials with better properties are prepared by this procedure than those formed by pure melt mixing of the corresponding homopolymers. A disadvantage of this process is the complicated and expensive start-up of production in comparison with other methods, eg, a melt mixing.

Another procedure for synthesis of polymer blends is formation of interpenetrating polymer networks. The network of one polymer is swollen with the other monomer or prepolymer; the monomer or prepolymer is then cross-linked (64). Blends of reactoplastics are prepared by this method.

4.2. Phase Structure Development in Molten State.

Starting Period of Melt Mixing. Most polymer blends are prepared by melt mixing and processed in the molten state. Therefore, the phase structure of a blend is formed during melt flow and it is petrified by solidification. Formation of the phase structure at the initial stage of the mixing was intensively studied by Macosko's group (65–68). It was found that sheets of the minor phase are formed after the start of mixing. Quite rapidly holes are formed in these sheets that coalesce. Further, the sheets transform to fibers or cocontinuous structures, which can become a dispersed structure (see Figs. 4**a**–**e**). If the softening or melting transition temperature of the minor phase is lower than that of the major phase, switching of phase continuity occurs at this stage of mixing (67). It was found that the reduction of characteristic size of phase domains from millimeters (characteristic size of polymer pellets) to micrometers is rapid. This reduction has been achieved during the first 2 min in batch mixers and in the first mixing zones in extruders.

Type of Phase Structure. For application of polymer blends, type and fineness of their phase structure are important. In blends of immiscible polymers 1 and 2 with a low content of 2, particles of component 2 are dispersed in the matrix of component 1. With a rising fraction of 2, a partially continuous structure of 2 appears. With a further increase in the amount of 2, a fully cocontinuous structure is formed. After that, phase inversion occurs, where 2 forms the matrix and 1 is the dispersed phase (69,70). Dependence of continuity indexes or percentages of continuity on volume fraction of component 2 is shown in Fig. 5. In contrast to low molecular weight emulsions, where phase inversion occurs in one point or in a very narrow interval of composition, the cocontinuous range for polymer blends is frequently quite wide. Phase inversion points calculated as the center of the interval with full cocontinuity of both the components and of the interval between critical volume fractions, $v_{\mathrm{cr}1}$ and $v_{\mathrm{cr}2}$ for starting continuity of components 1 and 2, need not be the same. The interval of volume fractions of the components in which the blend structure is cocontinuous depends on rheological properties of the components, interfacial tension, and mixing conditions. There have been several attempts to formulate a rule for prediction of the phase inversion point from the knowledge of viscosity of the components (69,71–74). They describe qualitatively the experimentally verified tendency of a less viscous



(a) (b)

(c) (d)

(e)

Fig. 4. (**a**) Scheme of initial morphology development. (**b**) Holes and lace structure observed in ribbons at 1.0-min mixing. (**c**) Broken lace structure and small spherical particles at 1.0-min mixing. (**d**) Morphology of the dispersed phase particles at 1.5-min mixing. (**e**) Morphology of the dispersed phase particles at 7-min mixing. (Reproduced with permission from Ref. 65).

component to be continuous down to low volume fractions, but all of them fail in the quantitative evaluation of a substantial part of experimental data (69). The proposed rules for prediction of the phase inversion from the knowledge of elastic properties of the components (75–77) contain unknown parameters or they have limited validity.

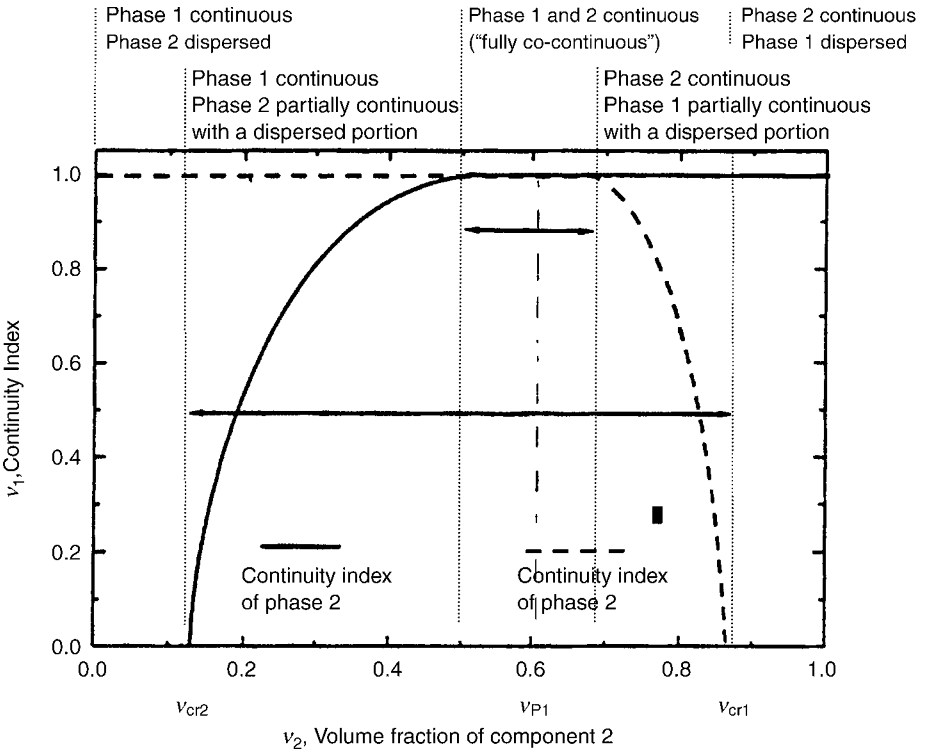


Fig. 5. Composition range of cocontinuous structure. Full line continuity index of phase 2, broken line continuity index of phase 1. v_{cr1}, v_{cr2}, v_{f1} a v_{f2} are volume fractions of phase 1 or 2 at which partial or full cocontinuity of the related phase start. The parameter v_{PI} designates phase-inversion composition. (Reproduced with permission from Ref. 69).

Utracki and Lyngaae-Jørgensen (78) proposed a theory based on the assumption that the critical volume fractions relate to the percolation thresholds of droplets and phase inversion appears at the composition at which the blend with dispersed component 1 and matrix 2 has the same viscosity as the blend with dispersed component 2 and matrix 1. The theory qualitatively describes dependences of the continuity indexes on the blend composition found experimentally. However, for some blends, v_{cr} does not relate to the percolation threshold for spheres and the predicted point of phase inversion does not agree with the experimental one for a number of systems.

A model for formation of fully cocontinuous morphology based on material properties and processing conditions was proposed (79). It is based on the assumption that full cocontinuity is achieved when randomly oriented cylindrical particles, formed by deformation of droplets of a minor component, are closely packed. For the volume fraction of a minor component, v_{dl} at which cocontinuous structure is formed, the following equation was derived

$$1/v_{d1} = 1.38 + 0.0213(\eta_m \gamma\, R_0/\sigma)^{4.2} \qquad (10)$$

where η_m is viscosity of the matrix, γ is the shear rate, σ is the interfacial tension and R_0 is the radius of equivalent sphere related to a droplet of the minor phase. The model qualitatively describes that the width of the cocontinuity interval increases with decreasing interfacial tension. Unfortunately, the model cannot be used in a predictive manner because R_0 has to be determined afterward.

Recent studies (80,81) showed that at long mixing in batch mixers, there is a transition from cocontinuous to dispersed morphology. The mixing time, at which the transition was determined, is about one order of magnitude longer than the time necessary for reduction of the characteristic size of phase domains from milimeters to micrometers. At present, it is not clear whether the cocontinuous structure is only transient or, in some cases, steady morphology. Elucidation of this problem is complicated by the fact that transitions between cocontinuous and dispersed structures frequently occur after a long period of mixing where it is very difficult to avoid strong degradation of the blend components.

In addition to cocontinuous morphology, also droplet-within-droplet (composite droplets, subinclusion, salami-like) morphologies are sometimes formed in blends with a higher content of minor component (70,82). In some systems, ribbonlike or stratified morphology was detected instead of the classic cocontinuous type (75). Rules for formation of individual types of morphology have not been formulated.

Prediction of the type of morphology in polymer blends containing three or more components is a more difficult task than that for binary blends. Generally, properties of the components, interfacial tensions between them, and mixing conditions should be considered. A quite successful predictive scheme was proposed for blends with matrix component 2 and two minor dispersed components 1 and 3. It was proposed (70,83) that component 3 encapsulates the component 1 if the spreading coefficient λ_{31} is positive. λ_{31} is defined as

$$\lambda_{31} = \sigma_{12} - \sigma_{32} - \sigma_{13} \tag{11}$$

where σ_{12}, σ_{32}, and σ_{13} are the interfacial tensions for each component pair. If spreading coefficient λ_{13} is positive, the component 1 encapsulates component 3. For both λ_{31} and λ_{13} negative, separated droplets of 1 and 3 are formed. The concept of spreading coefficients was extended taking into account the overall interface Gibbs energy by including interfacial area of each component (84). Predictions of these schemes agree in substantial part with experimental results (70,83–86), but the effect of rheological properties of the components on the type of phase structure was detected in some work (87–89). The results in Ref. 89 can be plausibly explained if effective interfacial tensions, relating to flow, and consideration of elasticity of the components were used in the predictive schemes. No rule for prediction of the continuity degree of the components is available for ternary blends.

5. Binary Polymer Blends

5.1. Size of Dispersed Droplets in Flow.

The effects of the properties of blend components and mixing conditions on fineness of the phase structure are well understood qualitatively for binary polymer blends with dispersed structure. It is broadly accepted that the size of dispersed droplets in flowing blends is controlled by the competition between the droplet breakup and coalescence (70,90–94). On the other hand, the droplet breakup and coalescence in blends with viscoelastic components are complex events only approximately described. Moreover, the flow field in mixing devices is also complex, which further complicates correct description of the phase structure development (70,92–94).

Deformation of a droplet in a flow field is controlled by the competition of the deforming stress, τ, setting on the droplet by external flow field and the shape conserving interfacial stress, σ/R, where R is the droplet radius (70, 90–96). For characterization of the deformation, the dimensionless capillary number, Ca, defined as $Ca = \tau R/\sigma$, is used. Above a critical value, Ca_c, the external stress overrules the interfacial stress, the droplet is stretched and finally breaks into fragments. For Newtonian droplets in a Newtonian matrix, Ca_c is a function of the ratio, $p = \eta_d/\eta_m$, of the viscosities of the dispersed phase and matrix. For blends with viscoelastic components, Ca_c is also a function of their elasticity parameters. A minimum Ca_c was found for η_d/η_m between 0.1 and 1 for shear and extensional flows. At shear flow, Ca_c gradually increases with decreasing p for $p < 0.1$. For $p > 1$, Ca_c steeply increases with increasing p and goes to infinity for $p \approx 3–4$. At extensional flow, the minimum is flat and an increase in Ca_c for high and low p is weak. For flow in mixing devices, the dependence of Ca_c on p lies between those for shear and extensional flow (94). Two main breakup mechanisms were recognized: stepwise, ie, a repeated droplet breakup into two fragments; and transient, where the droplet is stretched into a long fiber that bursts into a chain of small droplets (70,90,92–94,97). It seems that the stepwise mechanism operates for Ca only slightly higher than Ca_c and the transient mechanism for $Ca \gg Ca_c$. Other breakup mechanisms such as tip streaming (or erosion) of small droplets from the surface of deformed droplets and breakup into two main and several satellite droplets were detected (70,94–96). So far, the role of individual breakup mechanisms in complex flow fields generated in mixing devices has not been fully understood and it is the object of intensive investigation.

Flow-induced coalescence is caused by droplet collisions due to the difference in their velocities (91–94,98–100) (see Fig. 6). The coalescence is usually

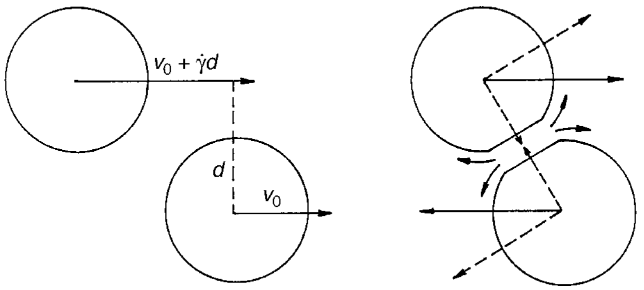


Fig. 6. Shear flow-induced coalescence of droplets with the same coordinate in neutral direction. Forces causing droplet approach and rotation in coordinate system moving with the center of inertia are indicating.

described in "ballistic approximation", ie, the number of fusions of droplets in a time period is expressed as a product of the number of collisions of noninteracting droplets and probability, P_c, that the collision will be followed by droplet fusion (91,92,94,100,101). A more or less intensive flattening of the droplets appears during their collision in dependence on properties of the blend components and flow field (100,102). Most calculations of P_c were focused on the case where droplets keep spherical shape during coalescence (102,103) or where the radius of flattened area is substantially larger than interdroplet distance (91,92,100). Unfortunately, the dependences of P_c on system parameters are quite different in these cases. In the former case, P_c is a decreasing function of p and the ratio of radii of large and small droplets and is independent of the average droplet size and deformation rate. On the other hand, in the latter case, P_c is independent of the ratio of droplet radii and depends on average R and the deformation rate. Therefore, inadequate application of any of these extreme cases can lead to a serious misinterpretation of experimental results. Recent calculations (104,105) have shown that for deformable droplets, P_c is given by the value for the spherical particles in the region of small R and steeply decreases at a certain R where a substantial flattening appears (for the shape of P_c, see Fig. 7). It should be mentioned that the theories developed so far describe dilute systems of Newtonian droplets in a Newtonian matrix. Simultaneous collisions of three and more droplets are not considered.

Generally, the distribution of droplet sizes in flow can be obtained as a solution of the generalized Smoluchowski (balance population) equation describing the competition between the droplet breakup and coalescence. Various approximate approaches to the solution of the equation with various expressions for breakup and coalescence frequencies were used in the literature (101,105–115). For rather long mixing in batch mixers, achievement of a steady state in the droplet size distribution is assumed. For mixing in extruders, development of the droplet size distribution during their throughput in individual zones of the extruders should be studied. A simplified model, where system of droplets is

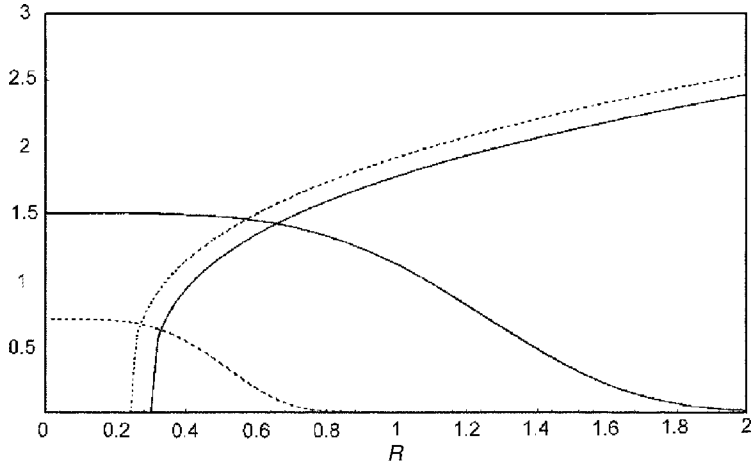


Fig. 7. Scheme of graphic solution of equation 12. Full and broken lines relate to blends with and without a compatibilizer. The Y-axis shows $F(R)$ and $(4/\pi)\gamma v P_c(R)$ in arbitrary units.

still monodisperse and breakup leads to a decrease and coalescence to an increase in droplet size, can be helpful in understanding the dependence of average droplet size on parameters of a system (116). The steady droplet radius for this model in shear flow can be calculated from the equation (116)

$$(dn/dt)_{\mathrm{B}} = (dn/dt)_{\mathrm{C}} \Rightarrow F(R) = (4/\pi)\gamma\ v\ P_{\mathrm{C}}(R) \tag{12}$$

where $(\mathrm{d}n/\mathrm{d}t)_{\mathrm{B}}$ and $(\mathrm{d}n/\mathrm{d}t)_{\mathrm{C}}$ are changes in the droplet number in a time unit due to their breakup and coalescence, respectively, and the breakup frequency $F(R) = 0$ for $R < R_{\mathrm{c}} = \sigma Ca_{\mathrm{c}}/(\eta_{\mathrm{m}}\gamma)$. The dependence of F on R for $R > R_{\mathrm{c}}$ has not been well established so far and very different expressions were used in literature (116). Based on recent results it appears that F increases with R slower than linearly (96,117). This assumption is in agreement with experimental findings that a steeper than linear increase in R with increasing v in a certain blend under constant mixing conditions occurs (70,90,93,94,116). In spite of the approximations used in the calculation of P_{c}, the shape of the dependence P_{c} on R is always similar to that in Fig. 7. It follows from graphic solution of equation 12, shown in Fig. 7, that for $R_{\mathrm{c}} < R$, at which P_{c} falls to very low value, steady state can be achieved during reasonable time. In the opposite case, regions of R exist, where only coalescence or practically only breakup occurs.

Under constant mixing conditions, an increase in average droplet radius with increasing volume fraction of the dispersed phase has been observed (70,93,94,99,106,118). The increase is a consequence of the breakup frequency in the first approximation is independent of v but the frequency of coalescence is an increasing function of v. An increase in interfacial tension leads to an increase in R (118) due to a decrease in Ca. The effect of viscosity ratio, p, can be directly studied by changing η_{d} while keeping η_{m} constant. For a system containing a low v, the effect of p on droplet breakup is decisive and the dependence of R on p for stepwise breakup is controlled by the dependence of Ca_{c} versus p. For a transient breakup mechanism, the situation is different and an increase in p can lead to smaller R also for $p > 1$ (91,92,112). Generally, P_{c} decreases with increasing p. Therefore, a lower R at $v \to 0$ and a steeper increase in R with v should appear for lower p if the stepwise breakup mechanism is decisive. This type of dependence was observed for polypropylene/ethylene–propylene elastomer blends mixed in the chamber of a Plasticorder (94,119). For the transient breakup mechanism, R should be smaller for larger p for all the volume fraction of the dispersed phase. If η_{m} is changed at a constant η_{d}, p and Ca are changed simultaneously. Mostly, an increase in η_{m} at constant η_{d} and mixing conditions leads to a decrease in the droplet size in the whole concentration range (94,119). The effect of elasticity of the components has not been fully understood so far. Available experimental results show that the deformation and breakup of droplets more elastic than the matrix are more difficult than in the related Newtonian system (70,120,121). Generally, the dependence of the droplet size on shear stress (mixing intensity) is affected by the concentration of the dispersed phase because R_{c} (R for $v \to 0$) depends on stress (deformation rate) in a different way than P_{c}. While R in dilute blends mostly decreases with increasing stress applied during mixing (94,122–124), in concentrated systems, R is a complex function of system parameters and it can be a decreasing, increasing, or nonmonotonic function of the applied stress (70,94,125,126). Only a weak dependence of R on processing parameters was quite frequently observed (70,127–129), apparently due to a non-Newtonian character of the matrix, increase in temperature in a mixer at growing mixing rate, and increasing P_c with decreasing R. Mostly, quite fine morphology is readily achieved after a short time of mixing in batch mixers or in first zones of extruders (64–68, 70,128–130). On the other hand, large particles of dispersed phase with high viscosity surrounded by material with fine phase structure were found in blends with low interfacial tension (94,131–133). Uniform fine morphology was achieved in these systems only after long and intensive mixing.

5.2. Phase Structure Evolution During Annealing. Substantial changes in the phase structure of molten blends of immiscible polymers appear at rest that are driven by the tendency to achieve a minimum interfacial area. Deformed droplets either retract to spheres or break up into smaller fragments. Relaxation occurs by one of several mechanisms, depending on initial deformation and the viscosity ratio (96,134,135). A droplet with the a/b less than ~ 9 retracts to a single sphere. Very elongated droplets of $\sim a/b > 60$, break up by capillary wave (Rayleigh) instability, ie, by the transient breakup mechanism mentioned above, into a chain of small droplets. In this case, the amplitude of perturbation wave grows exponentially with time and the growth rate increases with interfacial tension and decreases with viscosity of both the components and fibril radius (70,91–94,96). For droplets with intermediate deformation, the breakup is dominated by end pinching (96,134,135). Cocontinuous structures stay either cocontinuous and show increase in the phase size with time or break up into droplet/matrix morphologies (136,137). The breakup of fibers between crossing points of the structure is controlled by the capillary wave mechanism and it can occur if the length of fibers between the crossing points is substantially larger than the fiber thickness. Therefore, the coarsening of cocontinuous structures is typical of blends with compositions near 1/1 and their breakup appears for blends with asymmetric compositions. The coarsening rate increases with interfacial tension and decreases with viscosity of blend components (137). A substantial increase in the size of dispersed particles after annealing in the molten state was found for many polymer blends with particulate morphology (138). Two main mechanisms were suggested: coalescence driven by molecular forces and Brownian motion (139) and Ostwald ripening (140,141). Analysis of these mechanisms showed that the rate of coarsening should increase for coalescence and decrease for Ostwald ripening with increasing interfacial tension (138). A clear increase in the coarsening rate with interfacial tension was found experimentally (138). Moreover, coalescing droplets were detected in some experiments (142,143). Therefore, it seems that the coalescence induced by molecular forces and Brownian motion is the main mechanism of droplet coarsening, at least for blends with moderate or high interfacial tension.

6. Blends Containing a Compatibilizer

6.1. Effect of Compatibilizer on a Blend Microrheology. The presence of a compatibilizer at the interface substantially affects the development of the phase structure of molten blends in the flow and in quiescent state. The position and width of the concentration region related to cocontinuous morphology are affected by two competing mechanisms. A decrease in interfacial tension caused by a compatibilizer favors the formation and stability of cocontinuous structures. On the other hand, the compatibilizer suppresses the coalescence, which is assumed to be the cause for the cocontinuity formation (69). Experimentally, narrowing of the concentration region with cocontinuous structure was observed for some systems (69,144,145), but no change was found in other systems (69,146,147). Fixation of cocontinuous structure in a blend containing 20% of minor component by the addition of a compatibilizer was also observed (148).

The effect of a compatibilizer on fineness of the phase structure can be understood through its effects on the droplet breakup and coalescence. The decrease in interfacial tension mentioned above leads to a decrease in the critical droplet radius, R_c, at a constant Ca_c. Generally, Ca_c of a compatibilized blend differs from that of the related binary blend without compatibilizer (149,150). The bulk flow convects the compatibilizer toward the ends of the droplets causing a gradient in interfacial tension along the droplet surface. The lower interfacial tension on the tips promotes tip streaming which tend to reduce Ca_c. On the other hand, Marangoni stresses oppose deformation and an increase in the droplet surface due to deformation leads to compatibilizer dilution and, therefore, to an increase in interfacial tension. The last two effects tend to increase Ca_c (149,150). At breakup by the transient mechanism, a compatibilizer causes an increase in the breakup time due to a decrease in interfacial tension and existence of interfacial tension gradients (149–151). A decrease in interfacial tension due to the presence of a compatibilizer decreases the droplet radius R at which the probability of coalescence, P_c, falls to a negligible value. Two other mechanisms contributing to coalescence suppression were proposed (149,152). The first consists of immobilization of the interface (suppression of liquid circulation in droplet) due to the Marangoni stress. The Marangoni stress is induced by the convection of a compatibilizer out of the gap between approaching droplets, which leads to a gradient of interfacial tension (149,150). The immobilization of the interface decreases P_c for small R. The other mechanism, repulsion of the droplets arises mainly from the compression of the compatibilizer block extending into the matrix phase (149,152). This mechanism is applied only if the dilution of a compatibilizer in the gap between droplets is not large. The effect of a compatibilizer on the breakup frequency and P_c (decrease in interfacial tension and the Marangoni effect are considered) is schematically illustrated in Fig. 7. Figure 7 shows that the situation when steady state is not achieved is more probable for blends with a compatibilizer. In the calculation of steady R, changes in interfacial tension induced by changing interfacial area in the droplet breakup and coalescence should be considered (153). The above effect can be quantified if the distribution of a copolymer between the interface and bulk phases, relation between copolymer concentration at the interface and interfacial tension, and the rate of copolymer migration along the interface and between the interface and bulk phases are known.

6.2. Effect of the Compatibilizer Architecture. Compatibilization efficiency of various copolymers follows from their thermodynamic and microrheological effects. It has been generally accepted that the total molecular weight of the copolymer, molecular weight of its blocks, and their number are the main structural characteristics of the compatibilizer affecting the phase structure of the final blend. Some contradictory results were published on the effect of block copolymers with different numbers of blocks. In some literature reports, diblock copolymers have been found more efficient compatibilizers than triblock copolymers (51,154,155). In several other studies, the opposite results have been obtained (156,158). Still other state that there is no difference between diblocks and triblocks (159). Some newer articles show the compatibilizing efficiency of multiblock copolymers (160–162), which seems to be supported also by some theoretical works (163,164).

It has been believed that proper molecular weight of the copolymer blocks should be close to that of the relevant homopolymer. However, some results show that copolymers with differing lengths can be efficient compatibilizers. A complex situation occurs also when the copolymer blocks are not chemically identical with homopolymer chains, but only similar and, thus, they exhibit limited miscibility. Complexity of the problems has been showed in a number of studies.

A high molecular weight blend of *i*PS and *i*PP with of a *i*PS−*i*PP diblock copolymer, where the molecular weight of both blocks amounted to 150,000 has been successfully compatibilized (154). It has been shown that for polystyrene (PS)/polyolefin(PO) blends, even PE-*g*-PS graft copolymers, can be suitable compatibilizers (165).

Cavanaugh and co-workers (166) have studied the compatibilization efficiency of various styrene−butadiene copolymers in polystyrene (PS, $M_w = 202{,}000$)/ polybutadiene (PB, $M_w = 320{,}000$) blends. The most effective compatibilizer proved to be a long, asymmetric diblock ($M_w = 182{,}000$; PS content 30%), which could entangle in both homopolymer phases. Short diblock copolymers and most of the random copolymers were inadequate as interfacial agents. Moderate improvement in impact strength were observed for a S-B multiblock.

The effects of the block length and block number in linear S-B block copolymers on compatibilization efficiency in low molecular weight PS/PB blends were studied also by Horák and co-workers (167).

Segregation of a poly(2-vinyl pyrrolidone-*block*-styrene-d_8-*block*-2-vinyl pyrrolidone) (PVP-dPS-PVP) triblock and dPS-PVP diblock copolymers between the PS and PVP homopolymers was studied (168). Both the block copolymers show an increase in the interfacial excess beyond the saturation plateau, due to the condensation of copolymer micelles adjacent to the PS/PVP interface in the PS phase (Fig. 8). A significantly lower critical micelle condensation (CMC) was determined for the triblock copolymer when compared with the diblock. While the condensation of the diblock copolymer micelles at the PS/PVP surface occurs above the CMC, no such preferential segregation is observed for the triblock copolymer.

The compatibilization process becomes more complicated when one of the copolymer blocks is not completely miscible with the corresponding blend component, ie, interaction parameter $\chi > 0$. This problem has been studied in PS/PO blends compatibilized with various block copolymers, consisting of styrene and aliphatic hydrocarbon sequences different from the used polyolefin (161,162,169–173). It was found that in these blends, the most important factor controlling the localization of the block copolymers at the PS−PO interface is the

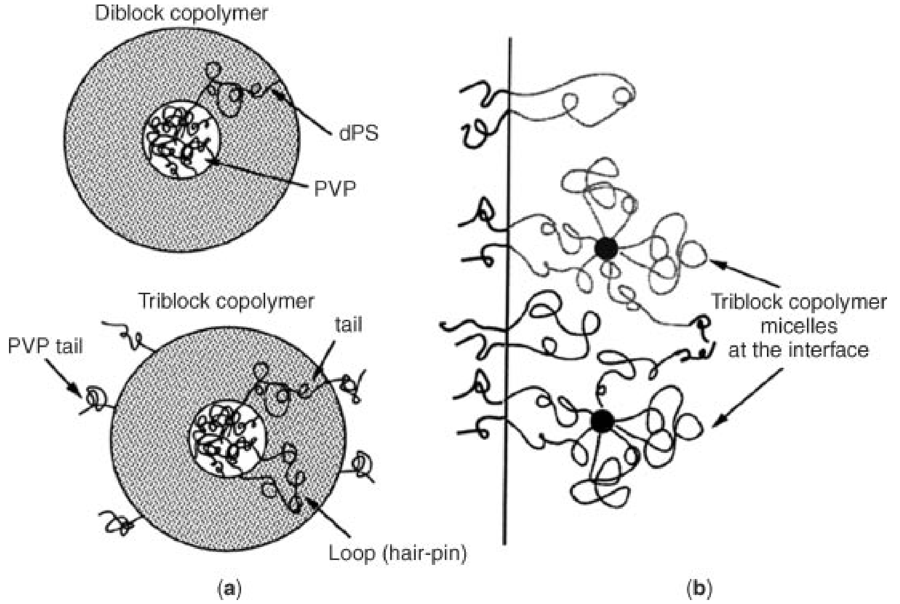
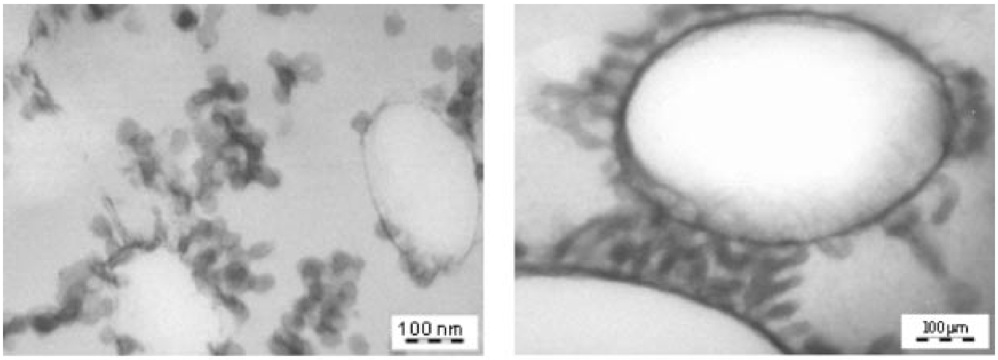


Fig. 8. Condensation of PVP-dPS-PVP triblock copolymer micelles adjacent to the PS/PVP interface in the PS phase. Schematics of (**a**) the isolated micelle structure for diblock and triblock copolymers and (**b**) triblock copolymer micelles adsorbed onto an interfacial brush of triblock copolymers. (Reproduced with permission from Ref. 168).

length of the styrene block in the block copolymers. Copolymers, having the styrene blocks long enough to form entanglements with the styrene homopolymer in the blend, are entrapped in the final compatibilized blends in this phase. Hence, their transport to the PS/PO interface is difficult and their compatibilization efficiency is low. Critical molecular weight for the formation of the entanglements of PS chains, M^*, cca 18,000 was determined (174,175). Surprisingly, in these blends, block copolymers with "long" styrene blocks are less efficient compatibilizers than those with "short" blocks.

Also the interfacial layer between the homopolymers differs in A/B + A-*block*-B′ blends from that in A/B + A-*block*-B blends. In blends compatibilized with block copolymers, having the corresponding blocks miscible with the blend components, they are supposed to be molecularly dispersed to a high degree at the A–B interface (Figs. 3,8). In A/B/A-*block*-B′ blends, block copolymers with "short" A blocks are localized at the A–B interface, too, but they do not lose their ordered supermolecular structure. Block copolymers having "long" A blocks are entrapped in the A homopolymer in the form of micelles or small particles, swollen by homopolymer chains (Fig. 9**a**). Additional annealing of these blends leads to pronounced migration of the entrapped copolymers to the A–B interface (Fig. 9**b**) and improvement of mechanical properties. On the other hand, coalescence and worsening of the A–B interface coverage were observed in annealed blends on addition of copolymers having "short" styrene blocks (169). In general, morphology of the A/B/A-*block*-B′ blends depends on the conditions of blend mixing and processing and cannot be predicted using the rules of equilibrium thermodynamics only. This dependence on the processing



(a) (b)

Fig. 9. Transmission electron microscopy (TEM) micrographs of the interface in PS/PP (4/1) blend with addition of 40S-60B-40S block copolymer: (**a**) as prepared sample; (**b**) annealed sample. (Reproduced with permission from Ref. 169.

conditions is more pronounced in blends with an excess of the A phase, ie, of the homopolymer that is fully miscible with one block of the block copolymer used (169).

Different behavior of block copolymers having blocks miscible with the corresponding homopolymers and those where one block differs chemically from the homopolymer was observed also by other authors (157,176–180).

In the PS/EPR blends, the S-B-S triblock copolymer with M_n value of the PS blocks equal to 7000 was found to be localized at the PS−EPR interface (179). The compatibilization efficiency of this block copolymer was further confirmed by finer dispersion in the resulting PS/EPR/S-B-S blends as well as by improved PS/EPR adhesion.

The compatibilization efficiency of block and graft copolymers is influenced by many factors, such as their chemical composition with respect to the character of the corresponding blend components, the number of the blocks, their molecular weights and, consequently, the total molecular weight. In blends where one block of a compatibilizer is not miscible, but only compatible with the coresponding blend component, achievement of thermodynamic equilibrium can be difficult since it depends on the processing conditions. However, it seems that the triblock copolymers can be considered the most efficient compatibilizers for most of the blends studied.

Despite extensive studies performed during more than three decades, no reliable rules for the prediction of the effect of molecular characteristics of block copolymers on the structure and properties of polymer blends have been formulated.

6.3. Effect of Compatibilizer Concentration. The compatibilizing efficiency of the copolymers is, besides the architecture, a function of their concentration. The effect of a compatibilizer concentration has been quantitatively characterized by the emulsification curve. The curve shows the dependence of the average particle diameter of the minor dispersed phase on copolymer concentration (70). The particle diameter decreases with increase of copolymer concentration until it reaches a constant value. For most systems, this value is achieved if the copolymer amount is 15–25% of the dispersed phase. There are systems where saturation was not detected until substantially higher concentration of a copolymer (181).

7. Structure Determination of Polymer Blends

Properties of polymer blends are closely associated with their structure on several scale levels, such as crystallinity and supermolecular structure of the blend components, and, of course, morphology of the final blend. Thus, a series of methods which enable to characterize these different structure parameters should be employed.

Wide angle X-ray scattering (waxs) affords information on the level of interatomic distances, ie, this method can be used for determination of crystalline modification in partly crystalline polymers, degree of the crystallinity, and also dimensions of the crystallites can be estimated from the width of the crystalline reflections (182). Small-angle X-ray scattering (saxs) experiments lead to determination of supermolecular structure, such as ordered two-phase separation in block copolymers (183,184), long period in semicrystalline polymers (185), or micellar structure (186,187). Classic experimental techniques used in saxs are reviewed in Ref. 188. Small-angle neutron scattering (sans), a related and often complementary method to saxs, is a very useful tool for determination of supermolecular structure in polymer blends (189). Moreover, by using sans, interactions in polymer blends can be studied if one of the blend components is deuterated in order to obtain scattering contrast (190). Recently, an ultrasmall-angle neutron scattering spectrometer (usans) was developed (191), lifting the upper resolution limit of saxs and sans instruments by an order of magnitude, and permitting thus an overlap with light scattering techniques.

The most suitable and comparatively rapid method used for determination of the morphology of polymer blends appears to be electron microscopy. Techniques employed in scanning electron microscopy (sem) have been reviewed (192). In addition to the use of sem for determination of particle size and shape in a blend, and adhesion between the blend components (193, Fig. 10), evolution of the structure in dependence on the processing conditions and homogeneity of the blend can be quickly studied (194, Fig. 11). Transmission electron microscopy

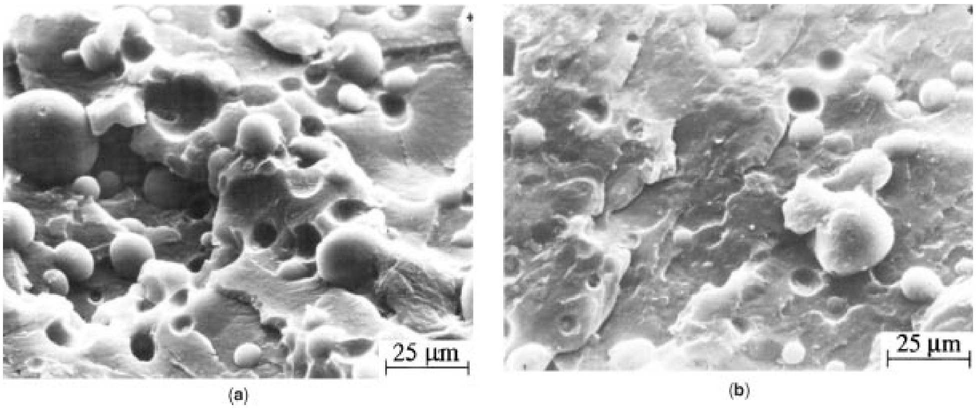


Fig. 10. Scanning electron micrographs of cryofractured surfaces of HDPE/HIPS (80/20) blend with H77 copolymer concentration of: (**a**) 0 wt%, (**b**) 5 wt%. (Reproduced with permission from Ref. 193).

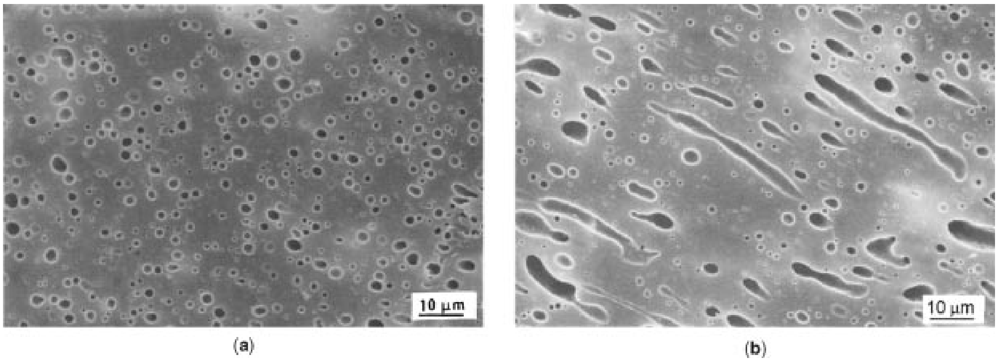


Fig. 11. Phase structure of PP/PS/SBS (71/24/5) blends mixed in microextruder at 250 °C for 2 min: (**a**) small particles; (**b**) large particles. (Reproduced with permission from Ref. 194).

is a much more time-consuming method. Polymer samples need to be stained with OsO_4 or RuO_4 in order to obtain sufficient contrast and, in addition, very thin sections are necessary (195,196). The simplest result obtained by means of tem is, similarly to sem, description of the blend morphology. However, there is a wider scale of possibilities, such as localization of a block copolymer used as a compatibilizer in blends of immiscible polymers (197). A published study of the development of the morphology of poly(2-vinyl pyrrolidone)-*block*-polystyrene *d*-*block*-poly(2-vinyl pyrrolidone (PVP-*block*-dPS-*block*-PVP) triblock copolymer at the PS/PVP interface, observed by tem is found in Ref. 198 (Fig. 12).

Light scattering can be used for determination of the blend morphology not only in the solid, but also in the molten state (199,200). This method was successfully used in detection of phase transitions in polymer blends and determination of changes in droplet size in immiscible polymer blends due to breakup and/or coalescence. In comparison with microscopic methods, scattering methods can easily examine larger blend volume and, therefore, give more reliable average values of morphological parameters. On the other hand, microscopic methods provide more straightforward and complex information (201).

Differential scanning calorimetry (dsc) is used especially for discrimination between miscible and immiscible polymer blends (202). One T_g depending on blend composition indicates a miscible system, two T_gs coinciding with related T_gs of the components indicate an immiscible blend, and two T_g' shifted to the direction of their average value are typical of partially miscible systems.

As polymer blends are very complex systems, a combination of different methods for complete description of their structure is of great importance. References 203–207 give several examples of combinations used.

Block copolymers, usually used as compatibilizers in additive compatibilization, are very often organized in an ordered supermolecular structure, manifesting itself by an interference maximum in the region of saxs (183,184). The compatibilization efficiency of a block copolymer is associated with its interaction with the blend components and, consequently, with the changes of its supermolecular structure. Hence, it is convenient to start the study of its struc-

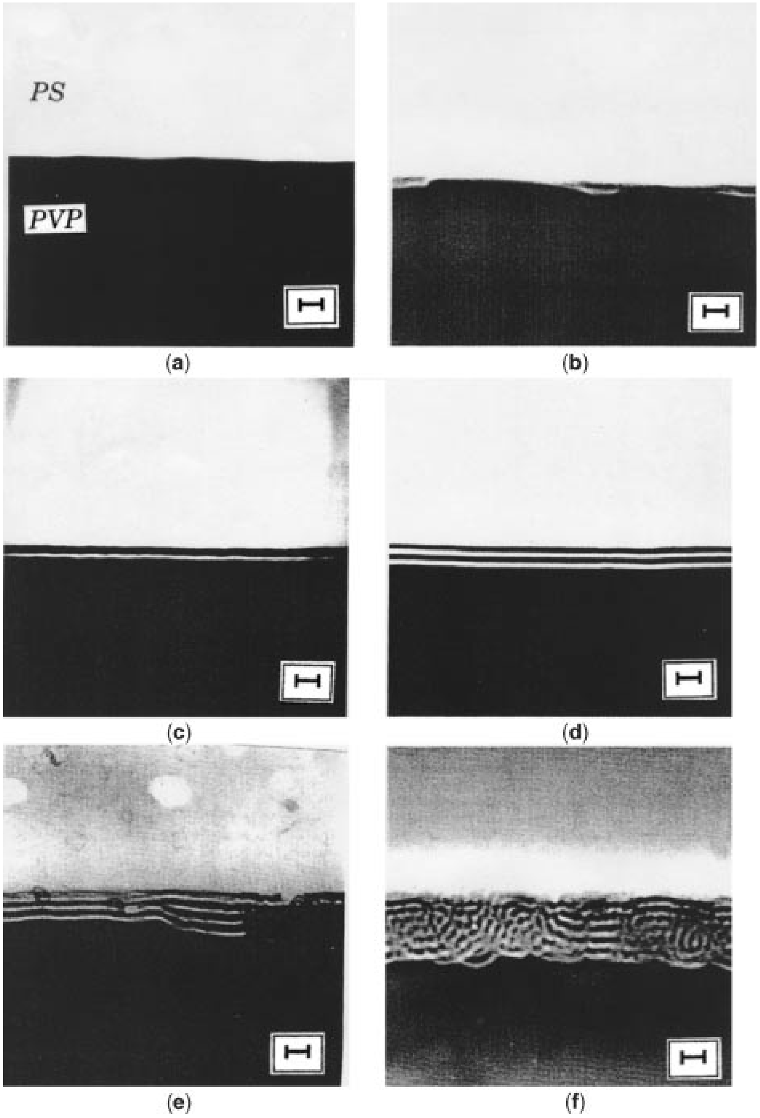


Fig. 12. The Tem micrographs of the morphology of the PVP-dPS-PVP triblock copolymer microstructure near the interface for (**a**) area chain density, $\sum = 0.09$, (**b**) $\sum = 0.17$, (**c**) $\sum = 0.22$, (**d**) $\sum = 0.4$, (**e**) $\sum = 0.6$, (**f**) $\sum = 1.0$ chains/nm^2. Note that disordered lamellae are found for $\sum > 0.6$ chains/nm^2. The bar scale denotes 100 nm. (Reproduced with permission from Ref. (198).

ture in compatibilized blends using saxs. This method gives information on a comparatively large sample volume, even if the information concerns the reciprocal space. Microscopic methods show the real structure, but of a very small part of the sample, which can be inhomogeneous. Combination of scattering and microscopic methods appears to be a very useful for investigation of the compatibilization process. Moreover, tem and sem experiments are relatively

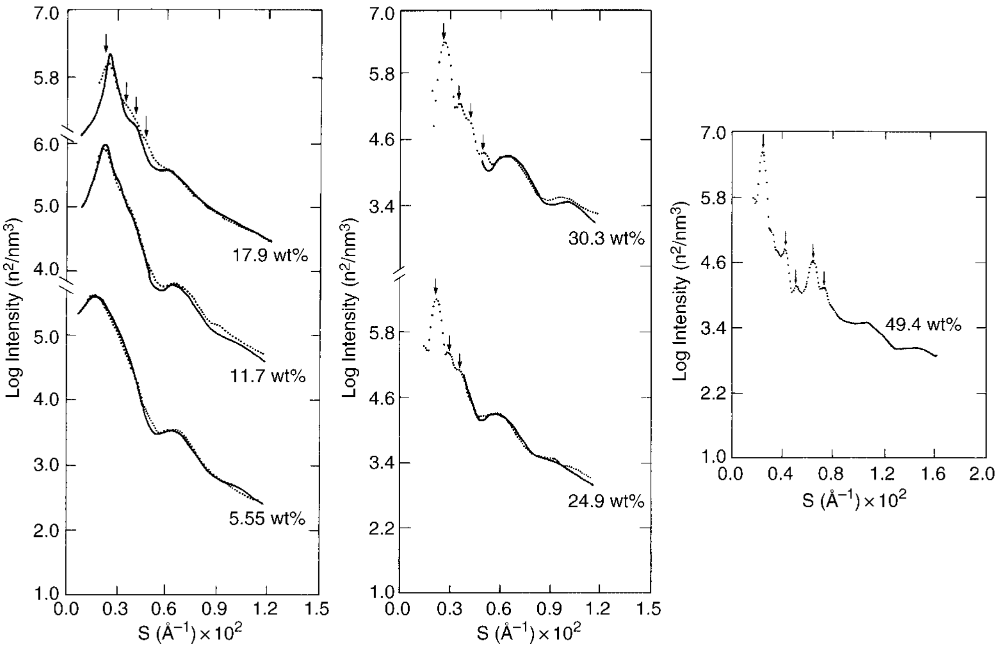


Fig. 13. The Saxs curves of blends consisting of copolymer SB 20/20 in 3900 PS homopolymer at various copolymer concentrations. (Reproduced with permission from Ref. 208).

time consuming, while measurement of one saxs curve takes several minutes. Thus, it is possible to check samples obtained under preparation conditions, when the steady state is achieved comparing of sax curves. Then, only several selected samples can be studied by electron microscopic methods (168). A very instructive comparison of different ordering of a styrene–butadiene block copolymer in styrene homopolymer as obtained by tem, together with corresponding saxs curves is found in Ref. 208 (Fig. 13).

8. Physical Properties of Polymer Blends

Preparation of heterogeneous polymer blends ranks among the effective ways of upgrading polymers and preparing new cost-effective materials. Tensile modulus E_b or shear modulus G_b, tensile yield strength σ_{yb}, tensile strength (stress at break) σ_{ub}, fracture resistance, permeability P_b to gases and vapors, etc, are viewed as very important physical properties, which simultaneously predetermine possible applications of the blends made of industrially useful polymers. Phase structure (morphology), which depends on blend composition, relative viscosities of components, interfacial energy, mixing machine and adopted conditions of the mixing process, annealing, reprocessing, etc is essential for the properties of heterogeneous melt-mixed blends consisting of immiscible or partly miscible polymers (209,210). As the phase structure of a blend formed in a mixing machine does not correspond to a state with the lowest Gibbs energy, the phase structure coarsening starts to take place immediately after completion of the mixing process, and is stopped only by freezing-in the melt. The coarsening process is reinitiated whenever blends are heated to the processing temperatures in the course of following operations, such as injection or compression molding, reprocessing, and quiescent annealing. In practice, the coarsening is undesirable phenomenon because it usually accounts for deterioration of mechanical properties of annealed or reprocessed blends.

Heterogeneous blends of immiscible or partially miscible polymers are isotropic heterogeneous materials with three-dimensional spatial continuity of one or more components (69,211). In binary blends, the cocontinuity (duality) of constituents occurs in the central composition interval delimited by the critical fractions $v_{1\mathrm{cr}}$ and $v_{2\mathrm{cr}}$ of the components (78,69,212,213). From the viewpoint of mechanical properties, blends can be divided into two basic categories: (*1*) at $v_1 < v_{1\mathrm{cr}}$ or $v_2 < v_{2\mathrm{cr}}$, the minority component is dispersed as spherical particles in the continuous majority component (matrix); (*2*) at $v_1 > v_{1\mathrm{cr}}$ and $v_2 > v_{2\mathrm{cr}}$, both components become partially continuous. As soon as the volume fraction of a component exceeds v_{cr}, continuous entities are formed in the mixed blend, but a spectrum of particles still coexists. With increasing volume fraction, the degree of continuity of the component increases, so that in a narrower interval delimited by the volume fractions $v_{1\mathrm{dl}} > v_{1\mathrm{cr}}$ and $v_{2\mathrm{dl}} > v_{2\mathrm{cr}}$ both components are fully cocontinuous (213–215). The coarsening process manifests itself by narrowing the interval of the phase duality and/or by an increase in the particle size of the minority component. Physical properties of solid heterogeneous blends primarily depend on respective properties of the components, frozen-in phase structure and interfacial adhesion. Typical dependencies of physical properties on the blend composition are schematically visualized in Fig. 14.

8.1. Predictive Formats for Selected Physical Properties. Tailoring of heterogeneous polymer blends with balanced physical properties for specific applications is a frequent task of materials engineering. A great number of heterogeneous polymer blends have been studied and reported in available literature. A review of empirical knowledge gathered so far is beyond the scope of this basic article. Instead, the existing means applicable in projecting polymer blends is outlined. To reduce experimental time and costs of a blend development, it is desirable to have reliable formats for the prediction of considered physical properties. Although modeling and simulations cannot fully replace experimental investigation, their role in the designing and structural analysis of blends is increasing.

Physical properties of blends consisting of a continuous matrix and one or more dispersed (discrete) components can be predicted by using adapted models proposed for particulate composite systems (216–220). Most of these models do not consider effects of the particle size, but only of volume fractions of components in the system. Thus, the increase in particle size due to particle coalescence is not presumed to perceptibly affect mechanical properties. The exception is fracture resistance, which is controlled by particle size and properties of dispersed rubbers. As polymer blends with three-dimensional (3D) continuity of two or more components are isotropic materials, simple parallel or series models or models for orthotropic or quasi-isotropic materials are not applicable. Physical properties of blends with partially cocontinuous constituents can be calculated by

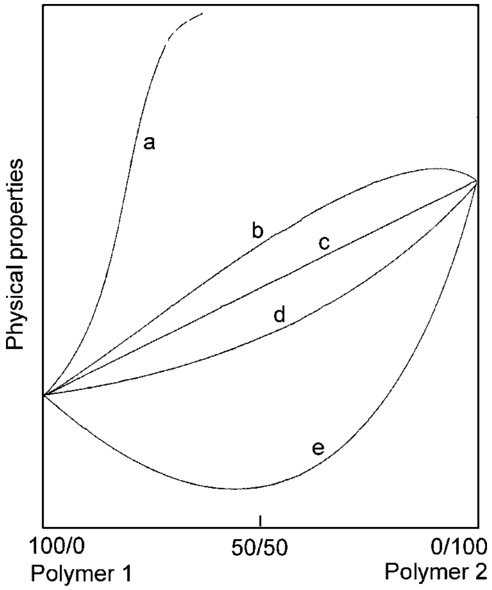


Fig. 14. Effect of the composition of heterogeneous binary blends on their physical properties: (**a**) fracture resistance, toughness and impact resistance of commercial rubber-toughened polymers; (**b**) modulus and tensile (yield) strength of blends consisting of partially miscible polymers; (**c**) density (straight line corresponds to the rule of mixtures); (**d**) modulus, compliance, tensile yield strength, stress at break, permeability to gases, thermal conductivity of compatible blends with good interfacial adhesion; and (**e**) tensile yield strength and stress at break of blends with poor interfacial adhesion; fracture and/or impact resistance of nontoughened blends.

means of a predictive format (221–223). The format is based on a two-parameter equivalent box model (EBM) (Fig. 15) and modified equations rendered by the percolation theory for two-component systems (78,212,224–227). This combination is necessitated by the fact that the EBMs are not self-consistent models. The EBM assumes that either component consists of a fraction continuous in the direction of the acting force (v_{1p} or v_{2p}) and a fraction discontinuous in that direction (v_{1s} or v_{2s}). In this concept, the lines of force do not cross any interface in the fractions v_{1p} and v_{2p}, while the phase continuity is completely disrupted in the fractions v_{1s} and v_{2s}, where all stress is transmitted through the present interfaces. Obviously, the continuity of blend components evaluated by means of extraction methods has a different meaning (69,210,228). The predictive format takes into account (*1*) the respective properties of components, (*2*) the cocontinuity interval of components, (*3*) interfacial adhesion, and (*4*) partial miscibility (if any) of components. Application of EBM to the prediction of physical properties of blends requires (*1*) to calculate the volume fractions v_{ij} and (*2*) to derive equations for the properties under consideration in terms of the EBM. Simultaneously predicted physical properties of blends are interrelated because they are calculated by using an identical set of input parameters characterizing a certain phase structure. The model is likely to fail if the blending process produces a significant change in the structure (eg, in crystallinity) and, consequently, in the considered properties of one or both constituents.

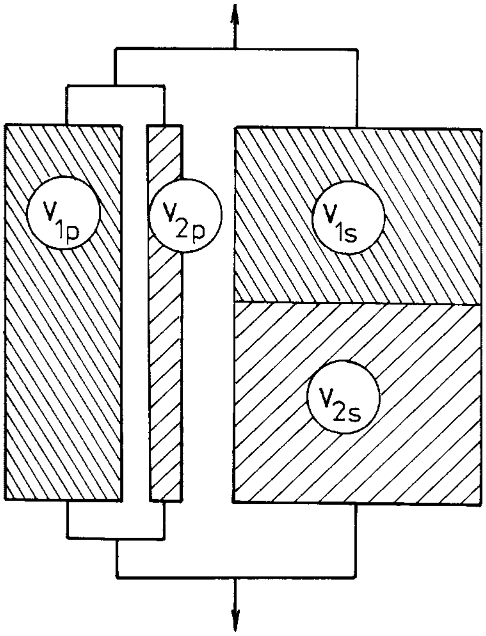


Fig. 15. Equivalent box model for a heterogeneous binary blend.

8.2. Calculation of the Volume Fractions in the EBM.

The EBM is a two-parameter model because of four volume fractions v_{ij} only two are independent; the volume fractions are shown in Fig. 15 are interrelated as follows:

$$v_1 = v_{1\mathrm{p}} + v_{1\mathrm{si}} v_2 = v_{2\mathrm{p}} + v_{2\mathrm{si}} v_1 + v_2 = v_\mathrm{p} + v_\mathrm{s} = 1 \tag{13}$$

The percolation theory (224–227) provides a universal formula for some physical properties of binary systems (modulus, permeability), where the contribution of the second component is negligible. The formula has been experimentally shown (212,229) to plausibly fit the modulus of model blends with $E_1 >> E_2$ in the range $v_{1\mathrm{cr}} \leq v_1 \leq 1$. Modifying this approach for binary blends, the following equations were derived (221–223):

$$v_{1\mathrm{p}} = [(v_1 - v_{1\mathrm{cr}})/(1 - v_{1\mathrm{cr}})]^q \tag{14a}$$

$$v_{2\mathrm{p}} = [(v_2 - v_{2\mathrm{cr}})/(1 - v_{2\mathrm{cr}})]^q \tag{14b}$$

where q is the critical exponent. The remaining $v_{1\mathrm{s}}$ and $v_{2\mathrm{s}}$ are evaluated using equation 13. The theoretical critical volume fraction (percolation threshold) $v_{\mathrm{cr}} = 0.156$ was calculated (78,219,226,227) for random spatial array of discrete spherical domains. Most reported values of q are located in the interval 1.6–2.0, which complies well with the theoretical prediction $q = 1.8$ (224,227). In a first approximation, "universal" values $v_{1\mathrm{cr}} = v_{2\mathrm{cr}} = 0.156$ and $q = 1.8$ can be employed in the EBM, which may provide a good prediction for blends whose components show similar viscosity and elasticity under mixing conditions.

Experimental values of $v_{1\mathrm{cr}}$ and/or $v_{2\mathrm{cr}}$ have mostly been found in the interval 0.15–0.25; however, extreme values ~0.03 or 0.46 have also been observed (230). Any considerable change in viscosity of one component influences both $v_{1\mathrm{cr}}$ and $v_{2\mathrm{cr}}$ (230,231), wherein the component with lower viscosity exhibits a stronger tendency to the continuity. This manifests itself in a lower v_{cr} and an asymmetric interval of the phase duality. Owing to enormous complexity, only a quantitative prediction of v_{cr} has only recently been attempted (213). This prediction is based on the rheological characteristics of components and of the blending equipment. Despite a number of simplifying assumptions, it provides useful guidelines for minimizing v_{cr} of one component in binary blends. In the marginal zone $0 < v_1 < v_{1\mathrm{cr}}$ (or $0 < v_2 < v_{2\mathrm{cr}}$), where only component 2 (or 1) is continuous, simplified relations can be used for the minority component in the EBM, ie, $v_{1\mathrm{p}} = 0$, $v_{1\mathrm{s}} = v_1$ (or $v_{2\mathrm{p}} = 0$, $v_{2\mathrm{s}} = v_2$), to obtain an approximate prediction of physical properties.

8.3. Moduli of Binary Heterogeneous Blends. A linear stress–strain relationship indispensable for modulus measurements is granted only at very low strains, typically <1%, where virtually all blends show interfacial adhesion sufficient for transmission of the acting stress. At strains exceeding the linearity limit, blend modulus (or compliance) decreases (or rises) with the strain. The tensile modulus of a two-component blend (Fig. 15) is given as (222)

$$E_{\mathrm{b}} = E_1\ v_{1p} + E_2\ v_2p + v_{\mathrm{s}}^2/[(v_{1\mathrm{s}}/E_1) + (v_{2\mathrm{s}}/E_2)] \tag{15}$$

where $v_{\mathrm{s}} = v_{1\mathrm{s}} + v_{2\mathrm{s}}$. Along with the tensile modulus from stress–strain measurements (Fig. 14, curve **d**), the storage modulus E_{b}' and the loss modulus E_{b}'' are frequently used. Dynamic mechanical thermal analysis (dmta) at a constant frequency is the case of steady-state harmonic conditions to which the elastic–viscoelastic correspondence principle is applicable (232). Thus isochronous dmta is a method allowing the use of the models for elastic materials and also for viscoelastic materials by replacing elastic constants by complex (viscoelastic) counterparts (233,234). Introducing $E_1{}^* = E_1{}' + \mathrm{i}E_1{}''$, $E_2{}^* = E_2{}' + \mathrm{i}E_2{}''$ and $E_{\mathrm{b}}{}^* = E_{\mathrm{b}}{}' + \mathrm{i}E_{\mathrm{b}}{}''$ into equation 15 and separating real and imaginary terms, one obtains

$$E_{\mathrm{b}}' = E_1'\ v_{1\mathrm{p}} + E_2'\ v_2p + v_{\mathrm{s}}^2\ N'/M \tag{16a}$$

$$E_b'' = E_1''\ v_1p + E_2''\ v_2\ p + v_s^2\ N''/M \tag{16b}$$

where

$$N' = v_{1s}\ E_1'\left(E'^2_2 +\ E''^2_2\right) + v_2s\ E_2'\left(E'^2_1 +\ E_1^{-2}\right) \tag{17a}$$

$$N'' = v_{1s}\ E_1''\left(E'^2_2 +\ E''^2_2\right) + v_2s\ E_2''\left(E'^2_1 +\ E_1^{-2}\right) \tag{17b}$$

$$M = (v_{1\mathrm{s}}\ E_2' + v_{2\mathrm{s}}E_1')^2 + \left(v_{1\mathrm{s}}\ E_2'' + v_{2\mathrm{s}}E_1''\right) \tag{17c}$$

A possible occurrence of an additional mechanical transition (loss peak) in the dynamic mechanical spectrum of polymer blends was ascribed to the geometrical arrangement of phases rather than to a molecular relaxation process within the interfacial area (235).

In boundary regions, ie, $v_1 < v_{1\mathrm{cr}}$ or $v_2 < v_{2\mathrm{cr}}$, the blend modulus can be calculated from the Kerner-Nielsen equation (216, 217, 219), Eq. 18a is for the dispersed component 2 with $E_2 > E_1$

$$E_{b1} = E_1(1 + A_1B_1v_2)/(1 - B_1\psi_2v_2) \qquad (18a)$$

The quantities A_1, B_1, ψ_2 are defined as follows:

$$A_1 = (7 - 5\mu_1)/(8 - 10\mu_1)$$

where μ_1 is the Poisson ratio of the (glassy) matrix

$$B_1 = (E_2/E_1 - 1)/(E_2/E_1 + A_1); \psi_2 = 1 + [(1 - v_{2\max})/(v_{2\max})^2]v_2$$

where $v_{2\max}$ is the maximum packing fraction of the dispersed particles (the value $v_{2\max} = 0.63$ for random close packing of monodisperse spheres is usually used (217).

If the component 1 with lower modulus E_1 is dispersed in a stiffer matrix 2, then inverted relations can be employed (216,217):

$$E_{\mathrm{b}2} = E_2(1 - B_2\psi_1v_1)(1 + A_2B_2v_1) \qquad (18b)$$

where

$$A_2 = (8 - 10\mu_2)/(7 - 5\mu_2);\ B_2 = (E_2/E_1 - 1)/(E_2/E_1 + A_2)$$

the formulas for ψ_1 and ψ_2 are analogous. Alternatively, other similar equations derived (218,219,236) for particulate systems can be used. The differences in moduli predicted by existing theories are not significant.

8.4. Compliance of Heterogeneous Binary Blends. As end products made of thermoplastics and their blends are frequently exposed to a long-lasting dead load, their resistance to creep becomes a significant characteristic of their dimensional stability. By introducing a cocontinuous creep-resistant component, the creep of blends can be substantially reduced. To anticipate the time-dependent compliance $D_{\mathrm{b}}(t)$ of a blend, the corresponding functions $D_1(t)$ and $D_2(t)$ of the components are to be experimentally evaluated. In analogy to the blend modulus (Fig. 14, curve **d**), the compliance of heterogeneous binary blends with cocontinuous components is as follows (237–239):

$$D_{\mathrm{b}}(t) = \{v_{1\mathrm{p}}/D_1(t) + v_{2\mathrm{p}}/D_2(t) + (v_{1\mathrm{s}} + v_{2\mathrm{s}})^2/[D_1(t)v_{1\mathrm{s}} + D_2(t)v_{2\mathrm{s}}]\}^{-1} \qquad (19)$$

To describe the compliance of blends with one continuous component and one discontinuous component, equation 19 can provide a first approximation by using $v_{1\mathrm{p}} = 0$, $v_{1\mathrm{s}} = v_1$ or $v_{2\mathrm{p}} = 0$, $v_{2\mathrm{s}} = v_2$. More accurate equations can be obtained by modifying previous equations (213). If the minority polymer 2 of the volume fraction v_2 having a lower compliance $D_2\ (t) < D_1\ (t)$ is dispersed in polymer 1, the compliance $D_{b1}\ (t)$ of the blend is (237)

$$D_{b1}(t) = D_1(t)[1 - B_1(t)\psi_2 v_2]/[1 + A_1 B_1(t) v_2] \tag{20a}$$

where

$$B_1(t) = [D_1(t)/D_2(t) - 1]/[D_1(t)/D_2(t) + A_1]$$

A_1 and ψ_2 are defined for equation 18a. If component 1 is dispersed in component 2, then the inverted relation applies:

$$D_{b2}(t) = D_2(t)[1 + A_2 B_2(t) v_1]/[1 - B_2(t)\psi_1 v_1] \tag{20b}$$

where

$$B_2(t) = [D_1(t)/D_2(t) - 1]/[D_1(t)/D_2(t) + A_2]$$

A_2 and ψ_1 are defined for equation 18b.

As the stress–strain linearity limit of most thermoplastics and their blends is very low, nonlinear viscoelastic behavior of heterogeneous blends is to be considered in most cases. The nonlinearity is at least partly ascribed to the fact that the strain-induced expansion of materials with Poisson's ratio <0.5 markedly enhances the fractional free volume (240). Consequently, the retardation times are perpetually shortened in the course of a tensile creep in proportion to the achieved strain. Thus, knowledge of creep behavior over appropriate intervals of time and stress is of great practical importance. The handling and storage of the compliance curves $D\ (t,\sigma)$ in a graphical form is impractical so that numerous empirical functions have been proposed (241), eg,

$$D(t,\sigma) = W(\sigma)(t/\tau_{rm})^n \tag{21}$$

where $W(\sigma)$ is a function of stress, τ_{rm} is the mean retardation time, and $0 \leq n \leq 1$ is the creep curve shape parameter reflecting the distribution of retardation times. Parameters characterizing the nonlinear compliance of the parent polymers can be extracted from generalized creep dependencies obtained by means of the time–strain superposition. The predictive format based on equations 14, 19, and 21 allows the prediction of corresponding parameters for blends and the construction of the creep curves of blends for selected stresses in the region of recoverable stress–strain behavior (238,239).

8.5. Yield and/or Tensile Strength of Heterogeneous Binary Blends. If blend components show yielding, usually at a strain of 3–6%, the yield strength in tension σ_{yb} of the resulting blend obeys the following equation derived in terms of the EBM in Fig. 15 (221,242):

$$\sigma_{yb} = \sigma_{y1} v_{1p} + \sigma_{y2} v_{2p} + A_{y1} v_s \tag{22}$$

where $\sigma_{y1} < \sigma_{y2}$ characterize the parent polymers and $0 \leq A \leq 1$ the extent of interfacial debonding. Two limiting values of σ_{yb}, identified with the lower or upper bound, can be distinguished by means of equation 22: (*1*) Interfacial adhesion is so weak that complete debonding occurs before yielding between the fractions of constituents coupled in series ($A = 0$ at the yield stress). As a function of blend composition, the lower bound of σ_{yb} passes through a minimum (Fig. 14, curve **e**). (*2*) Interfacial adhesion is strong enough to transmit the acting stress between constituents so that no debonding ($A = 1$) appears in the course of yielding; then the contribution of the series branch in the EBM is added to that of the parallel branch here the effect of different strain rates in the parallel and series branches on σ_{y1} and σ_{y2} is neglected. However, if two components differing in the yield strength are coupled in series, then this branch yields at σ_{y1} or σ_{y2}, whichever is lower. The upper bound of σ_{yb} is a monotonic function of the blend composition (Fig. 14, curve **d**). Whenever a partial or complete debonding occurs before yielding, then σ_{yb} passes through a minimum as a function of blend composition (211). A good correlation was found between the partial miscibility of blend components and their interfacial adhesion (243).

The yield strength σ_{yb1} of particulate systems, where dispersed particles do not yield and have a good adhesion to the matrix, is approximately equal to that of the matrix σ_{y1} (244). In the case of "zero" adhesion, the yield strength σ_{yb2} drops with the volume fraction of particles (219,245):

$$\sigma_{yb2} = \sigma_{y2}\left[1 - (v_1/v_{1\max})^{2/3}\right] \tag{23}$$

The latter formula also holds for glassy matrices with rubberlike inclusions, because yield strength of the dispersed component is negligible (219).

Equation 23 is suitable for the evaluation of the yield as well as tensile strength of particulate systems; equation 22 can be tentatively applied (221–223) for the tensile strength σ_{ub} of blends by replacing the yield strengths σ_{y1} and σ_{y2} by the tensile strengths σ_{u1} and σ_{u2}, respectively. If fracture mechanisms in the blend components are very different, the format may not fit the σ_{ub} versus v_2 dependence.

8.6. Application of the Predictive Formats.

In addition to the prediction of selected physical properties of envisaged blends, subsequent comparison of model calculations with experimental data allows the researchers (*1*) to analyze the phase structure of prepared blends, (*2*) to evaluate interfacial adhesion or the extent of interfacial debonding, (*3*) to assess to which extent the potential of a material has been exploited, etc. A great advantage of the EBM approach is that several physical properties can be simultaneously evaluated (222,223,246). If no information is available about the phase structure of blends, the properties can be predicted by using the "universal" values $v_{1cr} = v_{2cr} = 0.16$ and $q = 1.8$. However, this should be regarded as a first approximation, which may not approximate experimental data well because v_{1cr} and v_{2cr} of a studied system may be different, being affected by the relative viscosities of components, conditions of blend mixing, phase structure coarsening, etc. Conversely, as soon as some experimental data for a specific system are available, it is possible to determine actual $v_{1\mathrm{cr}}$ and $v_{2\mathrm{cr}}$ by a fitting procedure; thus the formats can be alternatively viewed as an efficient tool for analysis of the phase structure of blends. In a similar way, the phase structure of ternary blends (242,247) and/or the extent of interfacial debonding (248) can be evaluated. The outlined format for the modulus was successfully used in the structure analysis of interpenetrating epoxy and silica networks (249). Blends consisting of partially miscible polymers often show positive deviations (Fig. 14, curve **b**) of the moduli and yield strength (250,251). The deviations are ascribed to two effects: (*1*) respective properties of one or both conjugate phases are higher than those of parent polymers; (*2*) molecular mobility in conjugate phases is reduced due to associative interactions (heterocontacts) between the chains of components. The properties of these blends can be modeled by combining the predictive formats with an empirical equation expressing the composition of conjugate phases as a function of blend composition (251). The predictive format was also used for manifestation of the effects of the phase structure coarsening (narrowing of the cocontinuity interval) on the modulus, yield or tensile strength and gas permeability of heterogeneous polymer blends characterized by good or poor interfacial adhesion (252). If postmixing treatments account for a more profound drop in blend properties, then it is likely that, in addition to phase structure coarsening of the blend, the respective properties of constituents have deteriorated due to changes in their structure or due to chemical degradation.

8.7. Toughness of Polymer Blends. Toughness ranks among closely watched properties of polymer materials because it is an important prerequisite in most applications. It is commonly understood as the ability to resist fracture by absorbing mechanical energy (253–256). In general, toughness is an extremely complex phenomenon, depending on polymer composition, surface energy, density, crystallinity, modulus, yield strength as well as on testing conditions. Only parameters based on fracture mechanics can separate the effects of testing conditions from the effects of intrinsic material properties. Relevant material characteristics can be derived from either the energy balance approach or the stress intensity approach. Linear elastic fracture mechanics (LEFM), which is appropriate for (semi)brittle materials, operates with the strain energy release rate and the stress intensity factor. Nonlinear fracture mechanics (257,258) developed for ductile materials, including toughened polymers and blends, have introduced the J-integral fracture toughness, which can be considered as a nonlinear elastic energy release rate. A widely used method is that of the essential work of fracture (EWF), which is a material property related to the J-integral (255). Despite an enormous amount of empirical knowledge gathered so far, there are no means for quantitative anticipating the toughness of new materials.

Amorphous glassy polymers show two types of localized deformation mechanisms, ie, crazing and shear yielding (256,259–261). A craze can be described as a microcrack bridged by polymer fibrils (5−20 nm in diameter) partially bearing the load. Crazes initiated by pre-existing defects or flaws typically develop in a plane perpendicular to a maximum principal stress in polymers, whose crazing stress is lower than yield stress (262–264). Crazing involves formation of microvoids, which account for an increase in volume. Crazes grow through drawing of fibrils formed from the bulk polymer and at the final stage give rise to cracks at a stress below that necessary to cause bulk shear yielding.

The energy absorption per unit volume is relatively high within the craze deformation zone, but the amount of material involved in that absorption is very limited so that ensuing brittle fracture requires a very low mechanical energy. Brittle polymers have a low crack initiation energy (unnotched toughness) as well as a low crack propagation energy (notched toughness) (265). Brittle fracture is typical of PS, SAN, PMMA, and highly cross-linked glassy polymers (256,259,260).

Shear yielding involves localized or homogeneous plastic deformation occurring without any volume change. A number of glassy polymers possess some degree of ductility (at room temperature) at moderate rates of straining, eg, polycarbonate (PC), polysulfone, and polyethersulfone (260). Ductile fracture requires sufficient molecular (segmental) mobility for shear yielding to occur. Yielding localized in planar zones with high shear strains gives rise to “shear bands” at an angle of $\sim 45^\circ$ to the acting force, ie, in the direction of maximum shear stress. The strain hardening due to chain orientation eventually imposes a limit of the achievable plastic deformation. Ductile behavior is favored by uniaxial stress conditions, low strain rates, elevated temperature and smaller specimen cross-section (256,260). Ductile polymers have high crack initiation energy and low crack propagation energy (265,266). The transition between crazing and shear yielding is mainly predetermined by the entanglement and/or cross-linking density, because an increasing network density hampers the void formation in the process of crazing. Thus, the craze initiation stress is lower than the shear band initiation stress and crazing prevails in polymers with a network density lower than a critical value. Shear yielding is typical of highly entangled thermoplastics with flexible chains.

In semicrystalline polymers, the main energy-absorbing mechanism is shear yielding (261,267,268). Local crazing may take place as a part of the fracture process ahead of a running crack without being an important energy-absorbing mechanism. Semicrystaline polymers usually have high toughness at temperatures above their T_g. Their toughness decreases with increasing crystallinity and perfection of the crystallites because shear yielding is impeded. Rising spherulite size has negative effects on toughness because larger defects and voids are created and cracks propagate more easily along the interfaces between coarser spherulites. Higher molar mass accounts for the enhanced number of tie molecules between crystallites and spherulites, which improve the fracture resistance (260).

Molecular mobility, crazing and shear yielding are thermally activated rate processes, which follow the Eyring equation (256,264). For this reason all plastics are brittle under extreme testing conditions. The brittle/ductile transition temperature $T_{b/d}$ of a polymer means that at $T < T_{b/d}$ the fracture is brittle, while at $T > T_{b/d}$ the fracture is ductile. The transition is a consequence of the fact that the yield strength decreases faster with rising temperature than the brittle strength so that yielding starts to be a dominating deformation mechanism at $T > T_{b/d}$. This temperature, which is of major engineering importance, always lies below T_g. However, it increases with the strain rate, cross-linking density, presence of notches, etc (264).

Advanced characterization of the fracture processes in polymers and their blends is provided by the methods of fracture mechanics. A comprehensive review of this topic can be found in Refs. 253,255–259. Despite progress achieved in this field, the plastics industry traditionally employs standard empirical tests for evaluating toughness (259,269). The Charpy or Izod impact test and falling-weight impact tests are widely used although they provide only a semiquantitative basis for selection of materials. The impact resistance is a measure of the ability of a material to withstand the application of a sudden load without failure (259); however, it is not a material property because it depends on testing method and conditions, specimen geometry, and other factors. The obtained values are suitable for simple ranking of available materials or for evaluation of achieved improvements in material formulations. It is to be noted that it is extremely difficult to correlate the impact strength found for a type of specimens with the impact performance of the manufactured article (260). In practice it is advisable to select a method and testing conditions resembling the service conditions. Instrumented impact devices, which register the load-displacement curves in the course of impact, provide a deeper insight into the fracture mechanisms.

Toughening of rigid polymers consists in the involvement of their large fractions in energy absorption processes. To achieve this goal, a suitable amount of rubbery particles is to be evenly dispersed in the brittle matrix to function as stress concentrators and to initiate multiple energy-absorbing plastic microdeformations. A good dispersal of rubbery component and formation of an optimum size of particles are often aided by suitable compatibilization. During initial deformation, cavitation (formation of voids of the order of 10 nm) occurs within or around the rubber particles, which triggers either multiple crazing in polymers prone to crazing or shear deformations (bands) in shear-yielding matrices (256). Cavitation is an essential step in the toughening process, because it relieves the triaxial tension built up in the proximity of the crack tip. After cavitation, only biaxial tension remains, which is more favorable to shear yielding. A spectacular upswing in the toughness occurs at a certain rubber volume fraction, which indicates a percolation character of the underlying process. In this way, the toughness can routinely exceed by 1–2 orders of magnitude the value characterizing a neat rigid matrix (Fig. 14, curve **a**). However, in practice there is always a need to balance fracture resistance against other properties, eg, stiffness, resistance to creep and dimensional stability.

As the optimum fraction of the rubber component is rather low (0.05–0.30), the term "rubber-toughened polymers" (instead of "blends") is commonly used. Almost any engineering plastic can be made tougher in its rubber-modified version at the expense of modulus and yield strength. Although the mechanism of plastic deformation in such materials depends on the properties of matrix, dispersed rubber, and adopted test conditions, the fracture resistance of toughened polymers is primarily derived from the deformation and failure behavior of the rigid matrix, where most of the mechanical energy is absorbed via multiple crazing and/or shear yielding during straining and fracture. Semicrystalline polymers usually fracture in a ductile manner due to high resistance to crack initiation; however, in the presence of a sharp defect (notch) they show brittle fracture, because their resistance to crack propagation is low (255). For this reason, impact resistance of the notched test specimens is an important criterion of the achieved toughening. The quantitative theory of toughening based on the energy balance model (270) correctly predicts trends in the deformation and fracture behavior of toughened plastics with various structures. However, due to extreme complexity of the toughening phenomenon, to date there has been no format for the prediction of fracture resistance of rubber-modified plastics.

Rubber particle cavitation and subsequent multiple matrix crazing is the dominant mechanism of toughening in rubber-modified brittle matrices such as HIPS, SAN, PMMA [poly(methyl methacrylate)], and ABS polymer (260,271,272). In less brittle matrices, such as SAN and PMMA, mixed crazing and shear yielding can occur (265). In the beginning, application of external stress causes the biggest rubber particles to cavitate and initiate the first series of crazes, which grow by increasing their area and thickness. The rising deformation initiates secondary cavitation of smaller rubber particles and further crazing. Thus, crazes lying close to a craze plane begin to connect together; a rapid craze thickening follows, which involves drawing of fresh polymer from the walls of rising crazes. The latter stage can be identified with an effective energy-consuming process. Fibrillation occurs in an increasing fraction of rubber particles, which stretch in parallel with the crazes up to a saturation point. The rupture of a blend deformed by multiple crazing is assumed to be associated with failure in the fibrillated rubber particles when the local tensile strain exceeds their limiting value. The light scattering from microvoids formed in the matrix crazes and/or in the rubber particle cavities accounts for the stress whitening (273).

In HIPS, where the "salami" rubber particles consist of hard polystyrene subinclusions embedded in the matrix of crosslinked rubber, a specific type of cavitation was revealed (256). Cavitation in the rubber "membranes" results in a craze-like structure, where rubber fibrils form bridges between the PS subinclusions and between the subinclusions and the PS matrix. Yielding in the matrix allows the rubber fibrils to stretch and the rubber particles to expand until strain hardening stops the process. Also PVC and poly(oxymethylene) (POM) show very high values of the notched Izod toughness when the incorporated rubber forms an intermeshed (network) structure (265) instead of discrete particles. A higher effectivity of intermeshed rubber phase morphology was ascribed to a lower percolation threshold in comparison with that for an assembly of spherical particles. The toughening mechanism of ABS consists in the formation of numerous shear bands in addition to massive crazing (259). A similar effect can be produced in SAN by bimodal-sized rubber particles (265).

Shear yielding is the process by which most intrinsically ductile polymers achieve high strains. The incorporation of a rubbery component still enhances the toughness so that supertough materials can be produced (260,265,274), but the main purpose of the modification is to improve the resistance to crack propagation (259). The high stress concentrations generated in the matrix by rubber particles bring about a spectacular rise in the rate of plastic deformation because the adjacent matrix is free to yield and stretch in the way that was not possible in the neat matrix. The main factors controlling the shear yield stress of toughened plastics are the yield behavior of the rigid matrix and the volume fraction, shear modulus and particle size of the dispersed rubber. Essential gains in toughness are achieved only when the cohesive failure within the rubber particles induces accelerated shear yielding in the matrix, which is then followed by strain hardening of the yield zone due to stretching of both rubber and rigid matrix. In this plastic deformation process, chain segments slip past each other so that the material in the yield zone changes its shape, while only minor changes in density are due to disturbed molecular packing. Yielding localized in planar zones with high shear strains gives rise to pronounced shear bands; strain hardening due to the chain orientation eventually imposes a limit of the achievable plastic deformation. Toughening is particularly effective in the case of an array of closely spaced rubber particles, which assures that the ligaments between particles become fully yielded (256). The maximum degree of macroscopic toughness can be achieved if the local ligament thickness (surface–surface interparticle distance) decreases below its critical value (261,266), which is related to the experimental finding that brittle polymers become ductile below a critical specimen thickness of <1 μm. The critical ligament thickness is characteristic of the matrix for a given loading mode, temperature and rate of deformation (266).

Toughness of semicrystalline polymers is enhanced by means of techniques similar to those developed for glassy polymers (260,267,275). Rubbery particles usually initiate both massive crazing and shear banding, which depend on blend composition, morphology, rubber particle size and interfacial adhesion. An additional positive effect of the rubber component may consist in that its nucleating effect leads to finer spherulitic structure, thus improving the inherent toughness of the crystalline phase. Specific nucleating agents can markedly increase the toughness of the PP matrix by modifying crystalline structure and increasing the concentration of tie molecules (276,277).

Because of profound differences in the deformation and fracture behavior of polymer matrices, the optimum size of toughening rubber particles depends on the inherent fracture mechanism of a matrix. On the other hand, these optimum dimensions are affected by some properties of the used rubber, eg, modulus, viscosity and cross-linking density. Rubber particles of improper size are ineffective in the toughening process. The existence of a minimum particle size for efficient toughening corresponds to the minimum particle size required for cavitation (256). Extensive experimental work has established that the particle size of a toughener should lie within an optimum range. The optimum diameter of rubber particles for efficient toughening of brittle glassy polymers tending to craze decreases with their entanglement density (253,265).

A fine dispersion of rubber in a polymer matrix is facilitated by a low interfacial tension between blended components in the molten state. Under these conditions, the rubber particles may not be well bonded to the matrix for efficient stress transfer (54). Besides, the final particle size strongly depends on the rubber relative viscosity and blending conditions. The goal of concurrent optimizing dispersion and adhesion of a rubbery modifier is rather difficult to achieve. An elegant solution is offered by core-shell impact modifiers with a well-defined size and a narrow particle-size distribution (278). A major advantage of core-shell particles is that their size is set during their synthesis (emulsion polymerization) and remains the same after the dispersal in a host matrix. A soft core, made up of a rubbery polymer, is surrounded by a shell of grafted rigid polymer. The core of the particles provides the soft component that induces toughening mechanisms. The shell of a much higher T_g than the core has two primary functions: (*1*) to facilitate isolation of the particles from emulsion and to keep the cores from adhering to one another; (*2*) to act as the interlayer binding the matrix to the core.

A key factor in the performance of core-shell particles as impact modifiers is their adhesion to the host matrix, which is determined by the composition of both shell and matrix (278). If the latter polymers are compatible (miscible or partly miscible), the toughener will be effective. However, in most cases, the matrix and shell consist of dissimilar polymers. Also in this situation, solubilization of the matrix polymer into the grafted shell is to be ensured to develop proper interfacial adhesion. High degrees of the solubilization are favored by negative values of the interaction energy density, high molecular weight of the shell relative to the matrix, and a low shell thickness. If the matrix and shell are highly incompatible, introduction of a suitable compatibilizer can enhance the efficiency of core-shell impact modifiers. Alternatively, the matrix/shell adhesion can be enhanced by employing possible reactions between functional groups introduced in the shell and reactive sites of the matrix. Recent advances in polymerization techniques permit synthesis of various types of modified polyolefins (279) eg, polypropylene toughened with evenly distributed particles of ethylene–propylene rubber bound to the matrix.

The transition of dispersed particles from the rubbery to glassy state defines the lowest temperature at which the incorporated rubber is able to reduce the matrix yield stress and to account for significant toughening (280,281). The effect of added rubber usually fades away at temperatures 10–20 K above its T_g, which is manifested as a sharp drop in the fracture energy (256). An equation was derived for the brittle-ductile transition temperature as a function of the particle volume fraction, size, distribution and matrix ligament thickness (282). However, this critical temperature is also affected by testing conditions. In proportion to their fraction, rubbery impact modifiers reduce the modulus and yield strength of toughened polymers as quantified by equations 18b and 22, respectively.

Impact resistance of ductile polymers was also improved by blending with 5–15% of a brittle component (283,284). Although the enhancement of impact resistance is lower than in the ductile matrix/rubber systems, the advantage of rigid particles consists in a simultaneous increase in toughness and stiffness. To achieve these effects, brittle inclusions should be small and interfacial adhesion should be high. Then, the brittle inclusions having a sufficiently higher modulus and a lower Poisson's ratio than the matrix become ductile under the action of the compressive component of stress (285,286) and absorb mechanical energy. To prevent formation of a cocontinuous brittle component at its higher volume fractions, it is convenient to add two brittle and incompatible minority components. To achieve their separate dispersion, the surface energy of one minority component should be higher than that of the matrix, while the reverse relation holds for the other minority component (242). Ternary blends of polyamide 6 containing rigid particles of SMA ($\sim$5%) and particles of maleated ethylene–propylene rubber ($\sim$5%) are an example of blends with balanced mechanical properties (286,287). In these blends, the losses in stiffness and tensile strength caused by rubbery component are (more than) compensated by the action of the brittle component, while both minority components contribute to the toughness enhancement.

Recently, specific conditions have been elucidated under which isometric filler particles (eg, calcium carbonate) can account for a considerable toughening of PE (288) and PP (289). Polyamide 6/$CaCO_3$ (290) showed brittle behavior, probably due to a high plastic resistance of the matrix. In all cases, dispersal of fine filler particles and elimination of their agglomerates were critical for enhancing the toughness.

8.8. Rheological Properties of Molten Blends. The dependence of shear viscosity, first normal stress difference or storage modulus on blend composition varies very substantially from system to system. According to the type of relation between the logarithm of viscosity and concentration, blends were classified into four categories (291–293). Additive blends fulfil the log-additivity rule:

$$\log\ \eta = \sum_i v_i \log\ \eta_i \tag{24}$$

where v_i and η_i denote, respectively, volume fraction and viscosity of the component i. Other categories are blends showing a positive deviation from log-additivity, blends with a negative deviation and blends where both the positive and negative deviation have been observed. Because polymer blends are non-Newtonian liquids with η dependent on γ, dependences of η on the blend composition determined at a constant shear rate and at a constant shear stress can be different. Dependences at a constant stress are more plausible, because the stress is continuous at the interface in contrast with the deformation rate. Different types of the dependence of η on v at different shear stresses were found for some systems (291). Therefore, the above classification does not characterize polymer pairs only, but it is also a function of flow conditions. Dependences of the first normal stress difference and storage modulus on blend composition are similar to those for viscosity (291).

Generally, there is interrelation between rheological properties and morphology of flowing blends. Therefore, the morphology must be assumed in calculation of rheological properties or both characteristics must be calculated simultaneously. Great attention has been paid to the development of the theory of viscosity for blends containing a small amount of the dispersed component (96,291,292). A number of expressions for viscosity were derived using various approximations for these blends. For blends containing a very small volume fraction, v, of Newtonian droplets in the Newtonian matrix, the following equation was derived for $Ca \ll 1$.

$$\eta = \eta_m \left(1 + \frac{5p+2}{2p+2} v\right) \tag{25}$$

Equations considering somewhat higher contents of dispersed droplets, higher Ca and viscoelasticity of the components were derived. Also these expressions predict for blends containing dispersed droplets that viscosity of a blend is higher than that of its matrix also for $p \ll 1$. This is a general feature of all theories describing rheological properties of dispersed droplets in matrix and assuming stick condition at the interface.

The Palierne model (294,295) describes linear viscoelastic response of a dispersion of droplets, which are spherical in stress-free state. The model may account for viscoelastic properties of both matrix and droplets, effects of finite concentration, distribution of size and composition of the droplets and interfacial tension effects (also for compatibilized blends). The agreement of its predictions with experimental results is good (295). Description of rheological properties of blends with cocontinuous structure is more complicated.

A reasonable explanation of negative deviation of η from log-additivity rule (eq. 24) was proposed by Utracki (293). It is assumed that the interlayer slip at the interface should be considered in immiscible polymer blends. A semiempirical theory considering the emulsion behavior and interlayer slip factor can predict all the above mentioned categories of blend behavior with respect to log-additivity rule in dependence on the system parameters. Later, the origin of the slip at the interface was discussed in more detail (296). Suppression of the slip at the interface by the presence of a compatibilizer can explain the mostly observed higher viscosity of compatibilized blends than that of the related blends without compatibilizer (297). Most polymer blends have the dependence of shear viscosity on the shear rate similar to that of homopolymers only with a somewhat shorter Newtonian plateaus due to the effect of the interface (291,295). In contrast, dynamically vulcanized blends show yield stress, ie, a strong increase in η with decreasing shear rate in the region of low γ (298–300). It appears that the yield stress is induced by long-living entanglements between cross-linked domains of characteristic size of $\sim 1\ \mu\text{m}$.

8.9. Permeability of Blends to Gases and Vapors. The permeation of gases, vapors and liquids through films (layers, walls) of blends is of primary importance in many applications. The permeability of polymers is mainly determined by their polarity and crystallinity. Polyolefins are good barriers to moisture, but are highly permeable to hydrocarbons. On the other hand, aliphatic polyamides have outstanding resistance to hydrocarbons, but poor resistance to moisture. Thus, there are many reasons for blending various polymers to tailor materials with balanced and acceptable physical properties (301).

For a miscible polymer pair, the blend permeability P_b was empirically found to approximately obey the semilogarithmic additivity rule (302):

$$\ln P_b = v_1 \ln P_1 + v_2 \ln P_2 \tag{26}$$

where P_1 and P_2 are the permeabilities of components. In the free volume approach (303,304), it is assumed that the free volume of the mixture consists of the additive contributions from each component, which leads to the following equation:

$$\ln (P_b/Q) = [v_1/ \ln (p_1/Q)]^{-1} \tag{27}$$

where Q is a characteristic constant for the gas. The transport through blends consisting of miscible polymers is comprehensively reviewed in Refs. 301–303.

Heterogeneous blends of immiscible or partially miscible polymers are much more important engineering materials than homogeneous blends. The permeability of blends consisting of a continuous matrix and dispersed particles of another polymer can be approximated by models developed for particulate systems (301,302). However, these models (assuming dispersed components in the form of spheres, cylinders, cubes, lamellar structures of random orientation, etc) were found inadequate for the prediction of the blend permeability throughout the composition range (225,305–307), a part of which necessarily corresponds to blends with cocontinuous components. Thus, the EBM (Fig. 15) combined with the percolation approach was found (301) to be the most convenient predictive model for the permeability of heterogeneous blends. The permeability of binary blends consisting of partially continuous components can be predicted (223,230,308) using the format formally analogous to that for tensile modulus given in the previous section on mechanical properties (Fig. 14, curved **d**):

$$P_{\mathrm{b}} = (P_1 v_{1\mathrm{p}} + P_2 v_{2\mathrm{p}}) + v_{\mathrm{s}}^2/[(v_{1\mathrm{s}}/P_1) + (v_{2\mathrm{s}}/P_2)] \tag{28}$$

The data are usually presented as the relative permeability $P_{\mathrm{br}} = P_{\mathrm{b}}/P_1$ (relative to the component 1 with a lower permeability) versus blend composition. The "basic" curve calculated for $v_{1\mathrm{cr}} = v_{2\mathrm{cr}} = 0.16$ and $q = 1.8$ by means of equations 14 and 28 may deviate from experimental data if component 2 with a higher permeability, which controls P_{br}, is characterized by a $v_{2\mathrm{cr}}$ different from 0.16. Vice versa, it is possible to evaluate realistic values of $v_{1\mathrm{cr}}$ and $v_{2\mathrm{cr}}$ in individual series of blends by fitting experimental data. For the blends consisting of components, which differ by 2–4 orders of magnitude in their permeability, the semilogarithmic plot is more instructive (308). Moreover, it indicates $v_{2\mathrm{cr}}$ as a break (discontinuity) so that $v_{2\mathrm{cr}}$ can be adjusted with an accuracy of ~ 0.01. In this way, the format becomes an efficient tool for the analysis of the phase structure of polymer blends. In marginal regions $0 < v_1 < v_{1\mathrm{cr}}$ (or $0 < v_2 < v_{2\mathrm{cr}}$), simplified relations can be used for the EBM ie, $v_{1\mathrm{p}} = 0$, $v_{1\mathrm{s}} = v_1$ (or $v_{2\mathrm{p}} = 0$, $v_{2\mathrm{s}} = v_2$) to obtain an approximate prediction of permeability. The permeability of layered materials can be modeled as the series coupling of components.

The outlined format was found to match up well the permeability of a number of permeant-blend systems (230,308). The agreement with experimental data was very good throughout the composition range. Moreover, the format is suitable for simultaneous prediction or fitting of several physical properties, such as modulus and permeability (246) or modulus, tensile strength, and permeability (223).

9. Commercially Important Polymer Blends

There are three practical reasons for blending polymers: (*1*) Developing materials with desired properties, (*2*) extending performance of special expensive polymers by diluting it with a low cost polymer, and (*3*) utilizing plastic scrap by mechanical recycling. It is estimated that about one third of all commercially produced polymer materials are blends of two or more polymers. These multicomponent and mostly multiphase materials show various combinations of properties unattainable in any one polymer alone. Major concern is focused on increasing impact strength, processability, tensile strength, stiffness and heat resistance

(309). It should be emphasized that an improvement in one property leads mostly to deterioration of another property, and therefore the main efforts have been devoted to attain well ballanced properties of the final material required in pertinent application sphrere. Commercially produced polymer blends are the subjects of several excellent monographs (1,55,56,310–312). Thus only several examples of technically important polymer blends prepared by different compatibilization procedures are briefly presented below.

9.1. High Impact Polystyrene. Polystyrene shows excellent processability, good appearance, tensile strength, and thermal and electrical characteristics; however, its brittleness considerably limits its use in high-performance products. Therefore modification of its toughness made possible rapid growth of HIPS grades (60,272,313). Polystyrene whose impact strength is modified by the incorporation of rubber can be manufactured either by mechanical blending of components under controlled conditions or by grafting of the polymerizing styrene onto the rubber.

Mechanical blending of PS with PB is not very effective and in its classic form is a matter of the past. Blending technology is still used for modification of polystyrenes with special rubber components such as thermoplastic elastomers, eg, SBS or SEBS. High impact polystrene is sometimes blended with styrene homopolymer to yield the material at a reduced cost, but with acceptable intermediate properties for some applications.

At the present time, HIPS is produced by polymerization of styrene containing 5–10% of dissolved polybutadiene. The process yields both the styrene homopolymer and the polybutadiene-*graft*-polystyrene, where PS side chains are grafted onto the main polybutadiene chain. The process can be carried out technologically as mass (bulk) polymerization or as a mass suspension process, either batchwise or continuously. It is initiated thermally or by suitable initiator, such as dibenzoyl peroxide. As conversion reaches 2–3%, phase separation occurs as a result of immiscibility of PS and PB. The system forms so called polymeric oil-in-oil emulsion, in which the dispersed phase is a solution of PS in styrene and the continuous phase is a solution of PB in styrene. Grafted copolymer is formed at the interface and acts as an emulsion stabilizer. As the volume ratio of PS and PB in styrene approaches one, and the mixture is subjected to sufficiently strong shearing agitation and phase-inversion takes place. Sufficient agitation of the reaction mixture in the phase-inversion region is essential for morphology control of the final polymer blend. Particles of newly formed dispersed phase still contain permanently included residues of the original dispersed styrene phase as isolated particles. The presence of polystyrene subinclusions in polybutadiene particles is characteristic of HIPS. Impact strength is increased due to an increase in the effective volume of the PB phase. Near the completion of polymerization, cross-linking of the rubber component takes place. Rubber cross-linking must be sufficient to prevent disintegration during processing.

The HIPS performance is controlled by the amount and type of rubber, particle size distribution, rubber-phase volume, degree of grafting, and cross-linking as well as by molecular characteristics of the PS matrix. Most HIPS grades contain 5–7% of rubber, which covers the total volume fraction from 20 to 30%. For optimum toughening, rubber particles of several micrometers are required. For good surface appearance, a bimodal particle size distribution of rubber phase (eg, 2 and 0.2 μm) is desirable. The presence of a rubber phase in the PS matrix substantially improves not only impact strength but affects also other properties compared with styrene homopolymer. Thus elasticity modulus, tensile strength, and hardness somewhat decrease while elongation and melt viscosity increase. All things considered, HIPS shows a balanced complex of end-use properties, which is of advantage in a broad application sphere.

HIPS is processed by current procedures such as injection molding, extrusion, blow-molding, and thermoforming. These properties can be further modified by incorporation of special additives such as flame retardants, stabilizers, antistatic agents, etc. The main production fraction of HIPS is consumed in the manufacture of packaging materials, technical products, toys, and various consumer goods.

9.2. Acrylonitrile–Butadiene–Styrene Polymer. The ABS polymers are a family of thermoplastics with the san matrix containing dispersed elastomer particles. The oldest approach to ABS preparation, similarly as in the case of HIPS, is mechanical blending of individual components. At present, the graft polymerization of a mixture of styrene with acrylonitrile in the presence of a suitable rubber component is the current process. Most producers employ some form of emulsion technology, but the mass or mass-emulsion polymerization are also technologically feasible (60,272).

Common types of ABS have an average composition of 21–27% acrylonitrile, 12–25% butadiene and 54–63% styrene. The styrene component contributes good processability and stiffness of the final ABS, butadiene increases the impact strength and acrylonitrile improves chemical and heat deformation resistance. The two-phase system where rubber particles are dispersed in the matrix of san shows a morphology similar to HIPS but the particle size is smaller, and have also fewer san subinclusions than those in HIPS. The ABS polymer shows excellent toughness combined with good thermal and chemical resistance, high elastic modulus, and good appearance.

ABS can be processed by all common molding technologies. The main consumption of this polymer is for household appliances, automotive parts, business machine, telephone components, electrical devices, pipes and fittings, and leisure-time equipment.

9.3. Poly(2,6-dimethyl-1,4-phenylene oxide)/High Impact Polystyrene (PPO/HIPS). Poly (phenylene oxide) (PPO) is a polymer with high heat deformation resistance, excellent electrical properties, and high resistance to acids and bases. Because of high melt viscosity PPO is blended with styrene polymers to achieve rheological properties necessary for processing by current technologies. Improvement in PPO toughness is obtained simultaneously with a decrease in viscosity if HIPS is used as a modifier. Rubber particles distributed uniformly throughout the new matrix are responsible for an increase in toughness and polystyrene improves its processability. Unlimited PPO/PS miscibility enables preparation of blends with broad composition scale with well-balanced end-use properties. For high performance applications in electrotechnical and automotive industries, high impact blends of PPO with ABS, polyamides(PA), or PC are manufactured.

9.4. Polypropylene/Rubber. Polypropylene is a versatile polymer with good resistance to heat, chemicals, and solvents, and exhibits good electrical properties. Other properties can be improved by compounding with various nonpolymeric additives as well as with polymers. Blending with elastomers and copolymerizing with other monomers are used for toughening of this polymer (314,315). Synthetic elastomers as EPM, SEBS, PIB, and natural rubber are incorporated into PP matrix by mechanical blending. Especially PP/EPM blends are of considerable practical importance. These blends with a low content EPM are used as high impact polypropylene; the blends with high content of this elastomer can be used as thermoplastic elastomers. Phase structure control of modified PP depends strongly on molecular characteristics of the matrix, and therefore it is relatively difficult to achieve the desired and sufficiently stabile blend morphology. The presence of rubber particles in PP matrix increases the impact strength but leads to lower tensile strength, stiffness and heat deformation resistance. The complex of end-use properties is convenient mainly for application in automotive industry.

9.5. Poly(vinyl chloride)/Rubber.

Poly(vinyl chloride) (PVC) is an important commodity polymer with good chemical resistance and low flammability. Without modification, however, it is practically not processable and its mechanical properties and heat resistance are very poor. Therefore various additives as lubricants, stabilizers, and impact modifiers are incorporated to PVC grains to obtain versatile polymer.

To achieve good toughness, required for many applications, impact modifiers are added to PVC. Chlorinated polyethylenes, ethylene–vinyl acetate copolymers, styrene–methyl metacrylate grafted elastomers, vinyl rubbers, and polyacrylates are the most frequently used (316). These polymers are blended together with other additives. Blending conditions are very important for morphology control and consequently for the final properties of the blends.

Most high impact PVC blend production is consumed in civil engineering applications. Because of its low price and ability to be properly modified, this oldest commercially produced polymer remains one of the most important synthetic materials.

9.6. Polyamide/Rubber Blends.

The family of polyamides encompasses polymers with a variety of chemical compositions. Characteristic feature of these polymers is poor toughness at low temperature and/or in the presence of notches. Long-year effort to improve their toughness has resulted in numerous modification procedures (317). Most of them are based on melt blending of acid or anhydride-containing elastomers with PA. At present, producers of toughened PA use mostly rubbers containing small amount of maleic anhydride (up to 2%). During blending, reactive compatibilizarion takes place. The maleic anhydride groups react with amino groups of PA giving rise to graft copolymers at the interface. Saturated rubbers, eg, EPDM, SEBS, or BR are used. The obtained morphology shows the dispersed rubber particles of size between 0.001–0.1 μm. The compatibilization based on the reaction of anhydride and amino groups is also utilized for preparation of engineering materials as PA/PP, PA/ABS, or PA/PPO blends.

9.7. Polycarbonate Blends.

Polycarbonates are classified as construction plastics because of their high heat deformation temperature, electric properties, and mechanical characteristics including impact strength. Similarly as in the case of polyamides, they do not achieve the required toughness if notched or if they are exposed to low temperature. Therefore, polycarbonates are blended with ABS polymer to combine their properties with the toughness of ABS. No compatibilizer is needed in the blending of both the components because san and PC are partly miscible (313).

The PC/ABS blends are materials with an excellent combination of end-use properties, improved processability and, moreover, an acceptable cost. A broad scale of PC/ABS types is used in automotive industry and other engineering applications.

10. Recycling Polymers

Blending of polymers is important aspect of the recycling technologies that aim to overcome the problem of separation mixed polymeric waste into pure feedstock streams by direct processing of mixed materials with or without compatibilizers (318,319). Mechanical recycling of commingled plastic waste may be viewed as a compromise between conflicting requirements. That is, sorting of the waste is expensive, but can give recyclates of higher quality; on the other hand, reprocessing of commingled plastics is relatively inexpensive, but the resulting product shows lower mechanical and aesthetic properties. Under certain circumstances, the mechanical blending of mixed plastics waste can be advantageous from both the economical and ecological viewpoints.

For reprocessing of mixed plastics, either current processing machines or special machinery for manufacturing large profiles are used. The recyclates, called plastic lumber, suffer from inferior mechanical performance due to immiscibility, and so poor adhesion of components. Moreover, the presence of heterogeneities and particulate contamination restricts application of the products. Therefore, commingled plastics are often processed into large profiles which can rather fulfil requirements for strength characteristics. For manufacture of such profiles, specific procedures have been developed. Thus, eg, the intrusion process combines extrusion of mixed plastics with melt filling to a large mold without using screen-pack or an extrusion nozzle (Klobbie process) (319). Continuous extrusion produces linear profiles with large cross-sections of molten polymer materials that are extruded into cooled dies.

For more demanding applications, the commingled plastic wastes, as well as partially sorted plastics mixture, can be processed using compatibilizers. Recyclates with good mechanical properties as well as appearance are reported. Thus a mixture of polyolefins blended with organic peroxides or with a combination of peroxides and liquid PB gives materials of the same or higher impact resistance than virgin HDPE (57). A mixture of polyolefins and styrene plastics blended with a multicomponent compatibilizer (combination of SB and EPDM copolymers) shows excellent impact strength and acceptable other mechanical properties. Still better results have been obtained with a compatibilization system containing, besides copolymers, stabilizers based on aromatic amines. This combination shows even a synergistic effect (320). It seems that in this case the mixed polymers are not seriously damaged during their life cycle and the compatibilization and restabilization can be advantageous way of material recycling.

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