

# Polymer Mixtures

# 5

*Nature is a rag merchant who works up every shred and ort and end into new creations; like a good chemist whom I found the other day, in his laboratory, converting his old shirts into pure white sugar.*

—Ralph Waldo Emerson, *Conduct of Life: Considerations by the Way*, Chapter 5

## 5.1 Compatibility

The term *compatibility* is often assumed to mean the miscibility of polymers with other polymers, plasticizers, or diluents. Decisions as to whether a mixture is compatible are not always clear-cut, however, and may depend in part on the particular method of examination and the intended use of the mixture.

A common criterion for compatibility requires the formation of transparent films even when the refractive indices of the components differ. This means that the polymer molecules must be dispersed so well that the dimensions of any segregated regions are smaller than the wavelength of light. Such a fine scale of segregation can be achieved most readily if the components are miscible. It is possible, however, that mixtures that are otherwise compatible may appear not to be, by this standard, if it is difficult to produce an intimate mixture. This may happen, for example, when two high-molecular-weight polymers are blended or when a small quantity of a very viscous liquid is being dispersed in a more fluid medium.

Another criterion is based on the observation that miscible polymer mixtures exhibit a single glass transition temperature. When a polymer is mixed with compatible diluents the glass–rubber transition range is broader and the glass transition temperature is shifted to lower temperatures. A homogeneous blend exhibits one  $T_g$  intermediate between those of the components. Measurements of this property sometimes also show some dependence on mixing history or on solvent choice when test films are formed by casting from solution.

Heterogeneous blends with very fine scales of segregation may have very broad glass transition regions and good optical clarity. It is a moot point, then, whether such mixtures are compatible. If the components are not truly miscible,

the blend is not at equilibrium but the user may not be able to distinguish between a persistent metastable state and true miscibility.

Many investigators have opted to study polymer compatibility in solution in mutual solvents, because of uncertainty as to whether a bulk mixture is actually in an equilibrium state. Compatible components form a single, transparent phase in mutual solution, while incompatible polymers exhibit phase separation if the solution is not extremely dilute.

Equilibrium is relatively easily achieved in dilute solutions and studies of such systems form the foundation of modern theories of compatibility. Application of such theories to practical problems involves the assumption that useful polymer mixtures require the selection of miscible ingredients and that compatibility can therefore ultimately be explained in terms of thermodynamic stability of the mixture.

This assumption is not necessarily useful technologically. A more practical definition would consider components of a mixture compatible if the blend exhibits an initially desirable balance of properties that does not deteriorate over a time equal to the useful life that is expected of articles made from the mixture. Miscible mixtures are evidently compatible by this criterion. Compatibility is not restricted to such behavior since a blend of immiscible materials can be very useful so long as no significant desegregation occurs while the mixture is being mixed.

---

## 5.2 Thermodynamic Theories

The terminology in this area is sometimes a little obscure, and [Table 5.1](#) is provided to summarize the classification of solution types.

Thermodynamic theories assume that a necessary requirement for solution and compatibility is a negative Gibbs free energy change when the blend components are mixed. That is to say,

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0 \quad (5-1)$$

where the subscript m refers to the change of state corresponding to formation of the mixture and the other symbols have their usual significance. There will be no volume change ( $\Delta V_m = 0$ ) or enthalpy change ( $\Delta H_m = 0$ ) when an ideal solution is formed from its components. The properties of ideal solutions thus depend entirely on entropy effects and

$$\Delta G_m = -T\Delta S_m \quad (\text{ideal solution}) \quad (5-2)$$

### 5.2.1 Regular Solutions and Solubility Parameter

If  $\Delta H_m$  is not zero, a so-called regular solution is obtained. All deviations from ideality are ascribed to enthalpic effects. The heat of mixing  $\Delta H_m$  can be

**Table 5.1** Solution Behavior<sup>a</sup>

Solution type	$\Delta H_m$	$\Delta S_m$
Ideal	Zero	Ideal
Regular	Nonzero	Ideal
Athermal	Zero	Nonideal
Irregular	Nonzero	Nonideal

<sup>a</sup>The ideal entropy of mixing  $\Delta S_m$  is

$$\Delta S_m^{\text{ideal}} = -R \sum N_i \ln x_i \quad (5-3)$$

where  $x_i$  is the mole fraction of component  $i$  in the mixture and  $N_i$  is the number of moles of species  $i$ . Equation (5-3) represents the entropy change in a completely random mixing of all species. The components of the mixture must have similar sizes and shapes for this equation to be true.

formulated in terms of relative numbers of intermolecular contacts between like and unlike molecules. Nonzero  $\Delta H_m$  values are assumed to be caused by the net results of breaking solvent (1-1) contacts and polymer (2-2) contacts and making polymer–solvent (1-2) contacts [1,2].

Consider a mixture containing  $N_1$  molecules of species 1, each of which has molecular volume  $v_1$  and can make  $c_1$  contacts with other molecules. The corresponding values for species 2 are  $N_2$ ,  $v_2$ , and  $c_2$ , respectively. Each (1-1) contact contributes an interaction energy  $w_{11}$ , and the corresponding energies for (2-2) and (1-2) contacts are  $w_{22}$  and  $w_{12}$ . Assume that only first-neighbor contacts need to be taken into consideration and that the mixing is random. If a molecule of species  $i$  is selected at random, one assumes further that the probability that it makes contact with a molecule of species  $j$  is proportional to the volume fraction of that species (where  $i$  may equal  $j$ ). If this randomly selected molecule were of species 1 its energy of interaction with its neighbors would be  $c_1 w_{11} N_1 v_1 / V + c_1 w_{12} N_2 v_2 / V$ , where the total volume of the system  $V$  is equal to  $N_1 v_1 + N_2 v_2$ . The energy of interaction of  $N_1$  molecules of species 1 with the rest of the system is  $N_1/2$  times the first term in the previous sum and  $N_1$  times the second term [it takes two species 1 molecules to make a (1-1) contact]; i.e.,  $c_1 w_{11} N_1^2 v_1 / 2V + c_1 w_{12} N_1 N_2 v_2 / V$ . Similarly, the interaction energy of  $N_2$  species 2 molecules with the rest of the system is  $c_2 w_{22} N_2^2 v_2 / 2V + c_2 w_{12} N_1 N_2 v_1 / V$ . The total contact energy of the system  $E$  is the sum of the expressions for (1-1) and (2-2) contacts plus half the sum of the expressions for (1-2) contacts (because we have counted the latter once in connection with  $N_1$  species 1 molecules and again with reference to the  $N_2$  species 2 molecules):

$$E = \frac{c_1 w_{11} N_1^2 v_1 + w_{12} N_1 N_2 (c_1 v_2 + c_2 v_1) + c_2 w_{22} N_2^2 v_2}{2(N_1 V_1 + N_2 V_2)} \quad (5-4)$$

Equation (5-4) can be manipulated to

$$E = N_1 \left( \frac{1}{2} c_1 w_{11} \right) + N_2 \left( \frac{1}{2} c_2 w_{22} \right) + \frac{1}{2} \frac{N_1 N_2}{N_1 v_1 + N_2 v_2} \times [w_{12}(c_1 v_2 + c_2 v_1) - \omega_{11} c_1 v_2 - \omega_{22} c_2 v_1] \quad (5-5)$$

To eliminate  $w_{12}$  it is assumed that

$$\frac{1}{2} w_{12} \left( \frac{c_1}{v_1} + \frac{c_2}{v_2} \right) = \left[ \frac{c_1 w_{11}}{v_1} \frac{c_2 w_{22}}{v_2} \right]^{1/2} \quad (5-6)$$

In effect, this takes  $w_{12}$  to be equal to the geometric mean of  $w_{11}$  and  $w_{22}$ . Here, it is worth noting that the geometric mean assumption is only valid when the two species have comparable size and shape and interact with each other through dispersion forces. Then

$$E = N_1 \frac{c_1 w_{11}}{2} + N_2 \frac{c_2 w_{22}}{2} - \frac{N_1 N_2 v_1 v_2}{N_1 v_1 + N_2 v_2} \left[ \left( \frac{c_1 w_{11}}{2v_1} \right)^{1/2} - \left( \frac{c_2 w_{22}}{2v_2} \right)^{1/2} \right]^2 \quad (5-7)$$

The first two terms on the right-hand side of Eq. (5-7) represent the interaction energies of the isolated components, and the last term is the change in internal energy  $\Delta U_m$  of the system when the species are mixed. If the contact energies can be assumed to be independent of temperature, the enthalpy change on mixing,  $\Delta H_m$ , is then

$$\Delta H_m = \Delta U_m = \frac{N_1 N_2 v_1 v_2}{N_1 v_1 + N_2 v_2} \left[ \left( \frac{c_1 w_{11}}{2v_1} \right)^{1/2} - \left( \frac{c_2 w_{22}}{2v_2} \right)^{1/2} \right]^2 \quad (5-8)$$

The terms in  $(c_i w_{ii}/2v_i)^{1/2}$  are solubility parameters and are given the symbol  $\delta_i$ . It is convenient to recast Eq. (5-8) in the form

$$H_m = [N_1 N_2 v_1 v_2 / (N_1 v_1 + N_2 v_2)] [\delta_1 - \delta_2]^2 = (N_1 v_1 / V)(N_2 v_2 / V) [\delta_1 - \delta_2]^2 V = V \phi_1 \phi_2 [\delta_1 - \delta_2]^2 \quad (5-9)$$

where the  $\phi_i$  are volume fractions. Hence the heat of mixing per unit volume of mixture is

$$\Delta H_m / V = \phi_1 \phi_2 [\delta_1 - \delta_2]^2 \quad (5-10)$$

where  $V$  is the total volume of the mixture. For solutions, subscript 1 refers to the solvent and subscript 2 to the polymeric solute.

Miscibility occurs only if  $\Delta G_m \leq 0$  in Eq. (5-3). Since  $\Delta S_m$  in Eq. (5-3) is always positive (the  $\ln$  of a fraction is negative), the components of a mixture are assumed to be compatible only if  $\Delta H_m \leq T \Delta S_m$ . Thus solution depends in this analysis on the existence of a zero or small value of  $\Delta H_m$ . Note that this theory allows only positive (endothermic) heats of mixing, as in Eq. (5-10). In general,

then, miscibility is predicted if the absolute value of the  $(\delta_1 - \delta_2)$  difference is zero or small.

The convenience of the solubility parameter approach lies in the feasibility of assigning  $\delta$  values a priori to individual components of the mixture. This is accomplished as follows.

Operationally, the cohesion of a volatile liquid can be estimated from the work required to vaporize a unit amount of the material. In this process the molecules are transported from their equilibrium distances in the liquid to an infinite separation in the vapor. The cohesive energy density (sum of the intermolecular energies per unit volume) is at its equilibrium value in the liquid state and is zero in the vapor. By this reasoning, the cohesive energy density in the liquid state is  $\Delta U_v/V^0$ , in which  $\Delta U_v$  is the molar energy of vaporization and  $V^0$  is the molar volume of the liquid.

From inspection of Eq. (5-8), it is clear that the solubility parameter  $\delta$  is the square root of the cohesive energy density. That is,

$$\delta = (\Delta U_v/V^0)^{1/2} \quad (5-11)$$

If the vapor behaves approximately like an ideal gas

$$\delta^2 = (\Delta H_v - RT)/V^0 = (\Delta H_v - RT)\rho/M \quad (5-12)$$

where  $\rho$  is the density of liquid with molecular weight  $M$ . Thus the heat of vaporization  $\Delta H_v$  can serve as an experimental measure of  $\delta$ .

Cohesive energy densities and solubility parameters of low-molecular-weight species can be determined in a straightforward manner by direct measurement of  $\Delta H_v$  or by various computational methods that are based on other thermodynamic properties of the substance. A polymer is ordinarily not vaporizable, however, and its  $\delta$  is therefore assessed by equating it to the solubility parameter of a solvent in which the polymer dissolves readily. If dissolution occurs, it is assumed that  $\Delta H_m = 0$  and  $\delta_1 = \delta_2$  (Eq. 5-10). Experimentally,  $\delta$  is usually taken as equal to that of a solvent that will produce the greatest swelling of a lightly cross-linked version of the polymer or the highest intrinsic viscosity of a soluble polymer sample. These two experimental methods may, however, give somewhat different results for the same polymer, depending on the polarity and hydrogen-bonding character of the solvent. Such solvent effects are mentioned in more detail in Section 5.2.3.

A more convenient procedure relies on calculations of  $\delta$  values rather than experimental assessments. Solubility parameters of solvents can be correlated with the structure, molecular weight, and density of the solvent molecule [3]. The same procedure is applied to polymers, where

$$\delta = \rho \sum F_i/M_0 \quad (5-13)$$

In Eq. (5-13),  $\rho$  is the density of the amorphous polymer at the solution temperature,  $M_0$  is the formula weight of the repeating unit, and  $\sum F_i$  is the sum of all

**Table 5.2** Group Molar Attraction Constants [4]

Group	Molar attraction $F_i$ (cal/cc) <sup>1/2</sup> /mol	Group	Molar attraction $F_i$ (cal/cc) <sup>1/2</sup> mol
–CH <sub>3</sub>	148.3	–H acidic dimer	– 50.47
–CH <sub>2</sub> –	131.5	OH aromatic	170.99
>CH–	85.99	NH <sub>2</sub>	226.56
–C–with no H	32.03	>NH	180.03
CH <sub>2</sub> =olefin	126.54	>N–	61.08
–CH=olefin	121.53	C≡N	354.56
>CH=olefin	84.51	NCO	358.66
–CH=aromatic	117.12	–S–	209.42
–C=aromatic	98.12	Cl <sub>2</sub>	342.67
–O–(ether, acetal)	114.98	Cl primary	205.06
–O–(epoxide)	176.20	Cl secondary	208.27
–COO–	326.58	Cl aromatic	161.0
>C=O	262.96	Br	257.88
–CHO	292.64	Br aromatic	205.60
(CO) <sub>2</sub> O	567.29		
–OH–	225.84	F	41.33
Structure feature		Structure feature	
Conjugation	23.26	6-Membered ring	– 23.44
<i>Cis</i>	– 7.13	<i>Ortho</i> substitution	9.69
<i>Trans</i>	– 13.50	<i>Meta</i> substitution	6.6
4-Membered ring	77.76	<i>Para</i> substitution	40.33
5-Membered ring	20.99		

the molar attraction constants. A modified version of a compilation [4] of molar attraction constants is reproduced in Table 5.2.

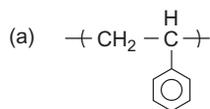
Examples of the use of the tabulated molar constants are given in Fig. 5.1. Such group contribution methods are often used in engineering estimations of other thermodynamic properties.

The solubility parameter of random copolymers  $\delta_c$  may be calculated from

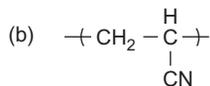
$$\delta_c = \sum \delta_i w_i \quad (5-14)$$

where  $\delta_i$  is the solubility parameter of the homopolymer that corresponds to monomer  $i$  in the copolymer and  $w_i$  is the weight fraction of repeating unit  $i$  in the copolymer [5]. Alternating copolymers can be treated by taking the copolymer repeating unit as that of a homopolymer (see Fig. 5.1c for example). No satisfactory method exists for assigning values to block or graft copolymers.

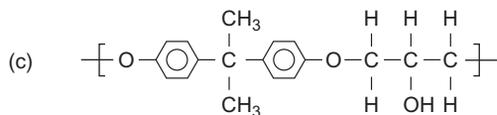
Mixtures of solvents are often used, especially in formulating surface coatings. It is not unusual to find that a mixture of two nonsolvents will be a solvent for a



Group	$F_i$	No. groups	$\sum F_i$	Description
—CH <sub>2</sub> —	131.5	1	131.5	Density = 1.05 g cm <sup>-3</sup>
>CH—	85.99	1	85.99	$M_r = 104 \text{ g mol}^{-1}$
—C=(aromatic)	117.12	6	702.72	$\delta = 1.05(896.77)/104$
6-membered ring	-23.44	1	-23.44	$= 9.0(\text{cal cm}^{-3})^{1/2}$
			896.77 $\left(\frac{\text{cal cm}^{-3}}{\text{mol}}\right)^{1/2}$	



Group	$F_i$	Description
—CH <sub>2</sub> —	131.5	Density = 1.18 g cm <sup>-3</sup>
>CH—	85.99	$M_r = 53$
CN	$\frac{354.56}{572.05}$	$\delta = (1.18)(572.05)/53$
		$= 12.7(\text{cal cm}^{-3})^{1/2}$



Group	$F_i$	No. groups	$\sum F_i$	Description
—CH <sub>3</sub>	148.3	2	296.40	Density = 1.15 g cm <sup>-3</sup>
—CH <sub>2</sub> —	131.5	2	263.0	$M_r = 284$
>CH—	85.99	1	85.99	$\delta = (1.15)(2572.44)/284$
—C— 	32.03	1	32.03	$= 10.4$
6-membered ring	-23.44	2	-46.88	
Para substitution	40.33	2	80.66	
—OH	225.84	1	225.84	
—O—(ether)	114.98	2	229.96	
—C=(aromatic)	117.12	12	1405.44	
			2572.44	

[Conversion factors:

$$1 \text{ MPa}^{1/2} = 1 (\text{J cm}^{-3})^{1/2}$$

$$= 0.49 (\text{cal cm}^{-3})^{1/2};$$

$$1 \text{ cm}^3 \text{ mol}^{-1} = 10^{-6} \text{ m}^3 \text{ mol}^{-1}]$$

FIGURE 5.1

Calculation of solubility parameters from molar attraction constants.

given polymer. This occurs if one nonsolvent  $\delta$  value is higher and the other is lower than the solubility parameter of the solute. The solubility parameter of the mixture  $\delta_m$  is usually approximated from

$$\delta_m = \delta_A \phi_A + \delta_B \phi_B \quad (5-15)$$

where the  $\phi$ 's are volume fractions.

It is believed that the temperature dependence of  $\delta$  can be neglected over the range normally encountered in industrial practice. Most tabulated solubility parameters refer to 25 °C.

Solubility can be expected if  $\delta_1 - \delta_2$  is less than about  $2(\text{cal cm}^{-3})^{1/2}$  [ $4(\text{MPa})^{1/2}$ ] and there are no strong polar or hydrogen-bonding interactions in either the polymer or solvent. Crystalline polymers, however, will be swollen or softened by solvents with matching solubility parameters but will generally not dissolve at temperatures much below their crystal melting points.

Table 5.3 lists solubility parameters for some common polymers and solvents. The units of  $\delta$  are in  $(\text{energy/volume})^{1/2}$  and those tabulated, in  $\text{cal}^{1/2} \text{cm}^{-3/2}$ , are called *hildebrands*. The use of the geometric mean expedient to calculate  $w_{12}$  in Eq. (5-6) in effect assumes that the cohesion of molecules of both species of the mixture is entirely due to dispersion forces, as mentioned. To allow for the influence of hydrogen-bonding interactions, it has been found useful to characterize solvents qualitatively as poorly, moderately, or strongly hydrogen-bonded. The solvents listed in Table 5.3 are grouped according to this scheme. Mutual solubility may not be achieved even if  $\delta_1 \simeq \delta_2$  when the two ingredients of the mixture have different tendencies for hydrogen bond formation.

The practice of matching solubility parameters and hydrogen-bonding tendency involves some serious theoretical problems, but it is useful if used with caution. For example, polystyrene, which is classed as poorly hydrogen-bonded and has a  $\delta$  value of  $18.4(\text{MPa})^{1/2}$ , is highly soluble in the poorly hydrogen-bonded solvents benzene and chloroform, both of which have matching solubility parameters. The polymer can be dissolved in methyl ethyl ketone ( $\delta = 19.0$  medium hydrogen bonding), but the latter is not nearly as good a solvent as either of the first pair. (The intrinsic viscosity of a polystyrene of given molecular weight is higher in chloroform or benzene than in methyl ethyl ketone.) On the other hand, poly(methyl methacrylate) has practically the same  $\delta$  as polystyrene but is classed as medium hydrogen-bonded. The two polymers are regarded as incompatible when both have high molecular weights, but benzene and chloroform do not seem to be weaker solvents than methyl ethyl ketone for poly(methyl methacrylate.)

Some of the problems noted here probably reflect the use of an oversimplified view of hydrogen bonding, in general. However, any attempt to correct this deficiency will most likely complicate the predictive method without a commensurate gain in practical utility. Improvements on the simple solubility parameter approach are summarized in Section 5.2.3.

**Table 5.3** Solubility Parameters

<b>(a) Solubility Parameters for Some Common Solvents (MPa)<sup>1/2a</sup></b>			
(i) Poorly hydrogen-bonded (generally hydrocarbons and derivatives containing halogen, nitrate, and cyano groups)		(ii) Moderately hydrogen-bonded (generally esters, ethers, ketones)	
<b>Solvent</b>	$\delta$	<b>Solvent</b>	$\delta$
<i>n</i> -Hexane	14.9	Diisodecyl phthalate	14.7
Carbon tetrachloride	17.6	Diethyl ether	15.1
Toluene	18.2	Isoamyl acetate	16.0
Benzene	18.8	Diocetyl phthalate	16.2
Chloroform	19.0	Isobutyl chloride	16.6
Tetrahydronaphthalene	19.4	Methyl isobutyl ketone	17.2
Methylene chloride	19.8	Diocetyl adipate	17.8
Carbon disulfide	20.5	Tetrahydrofuran	18.6
Nitrobenzene	20.5	Methyl ethyl ketone	19.0
Nitroethane	22.7	Acetone	20.3
Acetonitrile	24.4	1,4-Dioxane	20.5
Nitromethane	26.0	Diethylene glycol monomethyl ether	20.9
		Furfural	22.9
		Dimethyl sulfoxide	24.6
(iii) Strongly hydrogen-bonded (generally alcohols, amides, amines, acids)			
<b>Solvent</b>	$\delta$	<b>Solvent</b>	$\delta$
Lauryl alcohol	16.6	1-Butanol	23.3
Piperidene	17.8	Diethylene glycol	24.8
Tetraethylene glycol	20.3	Propylene glycol	25.8
Acetic acid	20.7	Methanol	29.7
Meta-cresol	20.9	Ethylene glycol	29.9
<i>t</i> -Butanol	21.7	Glycerol	33.8
Neopentyl glycol	22.5	Water	47.9
<b>(b) Solubility parameters of polymers (MPa)<sup>1/2</sup></b>			
<b>Polymer<sup>b</sup></b>	$\delta$	<b>H-bonding group<sup>c</sup></b>	
Polytetrafluoroethylene	12.7	Poor	
Polyethylene	16.4	Poor	
Polyisobutene	17.0	Poor	
Polypropylene	17.0	Poor	

<b>(b) Solubility parameters of polymers (MPa)<sup>1/2</sup></b>		
<b>Polymer<sup>b</sup></b>	<b><math>\delta</math></b>	<b>H-bonding group<sup>c</sup></b>
Polybutadiene	17.2	Poor
Polyisoprene	17.4	Poor
Poly(butadiene-co-styrene) 75/25	17.4	Poor
Poly(tetramethylene oxide)	17.6	Medium
Poly(butyl methacrylate)	18.0	Poor?
Polystyrene	18.4	Poor
Poly(methyl methacrylate)	19.0	Medium
Poly(butadiene-co-acrylonitrile) 75/25	19.2	Poor
Poly(ethyl acrylate)	19.2	Medium
Poly(vinyl acetate)	19.7	Medium
Poly(vinyl chloride)	19.9	Medium
Poly(methyl acrylate)	20.7	Medium
Polyformaldehyde	20.9	Medium
Ethyl cellulose	21.1	Strong
Poly(vinyl chloride-co-vinyl acetate) 87/13	21.7	Medium
Cellulose diacetate	23.3	Strong
Poly(vinyl alcohol)	26.0	Strong
Polyacrylonitrile	26.0	Poor
Nylon-6,6	28.0	Strong

<sup>a</sup>Selected data from Ref. [6].  
<sup>b</sup>Compositions of copolymers are in parts by weight.  
<sup>c</sup>The hydrogen-bonding group of each polymer has been taken as equivalent to that of the parent monomer. (The hydrogen-bonding tendency can be assigned qualitatively in the order alcohols > ethers > ketones > aldehydes > esters > hydrocarbons or semiquantitatively from infrared absorption shifts of CH<sub>3</sub>OD in a reference solvent and in the liquid of interest [7].)

### 5.2.2 Flory–Huggins Theory

Nonideal thermodynamic behavior has been observed with polymer solutions in which  $\Delta H_m$  is practically zero. Such deviations must be due to the occurrence of a nonideal entropy, and the first attempts to calculate the entropy change when long chain molecules are mixed with small molecules were due to Flory [8] and Huggins [9]. Modifications and improvements have been made to the original theory, but none of these variations has made enough impact on practical problems of polymer compatibility to occupy us here.

The Flory–Huggins model uses a simple lattice representation for the polymer solution and calculates the total number of ways the lattice can be occupied by small molecules and by connected polymer segments. Each lattice site accounts for a solvent molecule or a polymer segment with the same volume as a solvent

molecule. This analysis yields the following expression for  $\Delta S_m$ , the entropy of mixing  $N_1$  moles of solvent with  $N_2$  moles of polymer.

$$\Delta S_m = -R(N_1 \ln \phi_1 + N_2 \ln \phi_2) \quad (5-16)$$

where the  $\phi_i$  are volume fractions and subscripts 1 and 2 refer to solvent and polymer, respectively. The polymer consists of  $r_2$  segments, each of which can displace a single solvent molecule from a lattice site. Thus  $r_2$  is defined as

$$r_2 = M / \rho V_1^0 \quad (5-17)$$

where  $M$  is the molecular weight of the polymer that would have density  $\rho$  in the corresponding amorphous state at the solution temperature and  $V_1^0$  is the molar volume of the solvent. The number of lattice sites needed to accommodate this mixture is  $(N_1 + N_2 r_2)L$ , where  $L$  is Avogadro's constant.

Equation (5-16) is similar to Eq. (5-3), except that volume fractions have replaced mole fractions. This difference reflects the fact that the entropy of mixing of polymers is small compared to that of micromolecules because there are fewer possible arrangements of solvent molecules and polymer segments than there would be if the segments were not connected to each other.

Equation (5-17) applies also if two polymers are being mixed. In this case the number of segments  $r_i$  in the  $i$ th component of the mixture is calculated from

$$r_i = M_i / \rho_i V_r \quad (5-17a)$$

where  $V_r$  is now a reference volume equal to the molar volume of the smallest polymer repeating unit in the mixture. The corresponding volume fraction  $\phi_i$  is

$$\phi_i = N_i r_i / \sum N_i r_i \quad (5-18)$$

The entropy gain per unit volume of mixture is much less if two polymers are mixed than if one of the components is a low-molecular-weight solvent, because  $N_1$  is much smaller in the former case.

To calculate  $\Delta H_m$  (the enthalpy of mixing) the polymer solution is approximated by a mixture of solvent molecules and polymer segments, and  $\Delta H_m$  is estimated from the number of 1, 2 contacts, as in Section 5.2.1. The terminology is somewhat different in the Flory–Huggins theory, however. A site in the liquid lattice is assumed to have  $z$  nearest neighbors and a line of reasoning similar to that developed above for the solubility parameter model leads to the expression

$$\Delta H_m = zw(N_1 + N_2 r_2) \phi_1 \phi_2 L \quad (5-19)$$

for the enthalpy of mixing of  $N_1$  moles of solvent with  $N_2$  moles of polymer. Here  $w$  is the increase in energy when a solvent-polymer contact is formed from molecules that were originally in contact only with species of like kind.

Now the Flory–Huggins interaction parameter  $\chi$  (chi) is defined as

$$X = zwL / RT \quad (5-20)$$

This dimensionless quantity is the polymer–solvent interaction energy per mole of solvent, divided by  $RT$ , which itself has the dimensions of energy. Since  $\varphi_1 = N_1/(N_1 + N_2r_2)$ , Eq. (5-19) can be recast to give the enthalpy of forming a mixture with volume fraction  $\varphi_2$  of polymer in  $N_1$  moles of solvent as

$$\Delta H_m = RT \chi N_1 \phi_2 \quad (5-21)$$

The total volume  $V$  of this solution is  $(N_1 + N_2r_2)V_1^0$ , where  $V_1^0$  is the molar volume of the solvent. Then the enthalpy of mixing per unit volume of mixture is

$$\frac{\Delta H_m}{V} = \frac{RT \chi N_1 \phi_2}{(N_1 + N_2r_2)V_1^0} = \frac{RT \chi \phi_1 \phi_2}{V_1^0} \quad (5-22)$$

If the Flory–Huggins value in Eq. (5-22) is now equated to the solubility parameter expression of Eq. (5-10), it can be seen that

$$\chi = V_1^0(\delta_1 - \delta_2)^2/RT \quad (5-23)$$

Equation (5-23) suffers from the same limitations as the simple solubility parameter model, because the expression for  $\Delta H_m$  is derived by assuming that intermolecular forces are only nondirectional van der Waals interactions. Specific interactions like ionic or hydrogen bonds are implicitly eliminated from the model. The solubility parameter treatment described to this point cannot take such interactions into account because each species is assigned a solubility parameter that is independent of the nature of the other ingredients in the mixture. The  $\chi$  parameter, on the other hand, refers to a pair of components and can include specific interactions even if they are not explicitly mentioned in the basic Flory–Huggins theory. Solubility parameters are more convenient to use because they can be assigned *a priori* to the components of a mixture.  $\chi$  values are more realistic, but have less predictive use because they must be determined by experiments with the actual mixture.

From Eqs. (5-16) and (5-21) the Gibbs free energy change on mixing at temperature  $T$  is

$$\Delta G_m = \Delta H_m - T\Delta S_m = RT(\chi N_1 \phi_2 + N_1 \ln \phi_1 + N_2 \ln \phi_2) \quad (5-24)$$

Now, since

$$\left(\frac{\partial \Delta G_m}{\partial N_1}\right)_{T,P,N_2} = \left(\frac{\partial G_{\text{solution}}}{\partial N_1}\right)_{T,P,N_2} - \left(\frac{\partial G_1^0}{\partial N_1}\right)_{T,P,N_2} = RT \ln a_1$$

then

$$\left(\frac{\partial G_m}{\partial N_1}\right)_{T,P,N_2} = \mu_1 - G_1^0 = RT \ln a_1 \quad (5-25)$$

where  $a_1$  is a fictitious concentration called activity mentioned in Section 3.1.4. Thus, the difference in chemical potential of the solvent in the solution ( $\mu_1$ ) and in the pure state at the same temperature ( $G_1^0$ ) (i.e.,  $RT \ln a_1$ ) can be expressed in

terms of  $\chi$  by differentiating Eq. (5-24) with respect to  $N_1$ . Here,  $a_1$  and  $\chi$  are related by the following equation:

$$\ln a_1 = \ln \phi_1 + \left(1 - \frac{1}{r_2}\right) \phi_2 + \chi \phi_2^2 \quad (5-26)$$

Experimentally,  $\mu_1 - G_1^0$  can be obtained from measurements of any of several thermodynamic properties of the polymer solution [e.g., osmotic pressure as shown in Eq. (3-15)]. It can be shown then that the second virial coefficient (Eq. 3-24) is given by

$$A_2 = (0.5 - \chi) / \rho^2 V_1^0 \quad (5-27)$$

where  $\rho$  is the polymer density at the particular temperature. Since  $A_2 = 0$  in theta mixtures (Section 3.14) where the polymer is insoluble, the condition for compatibility is  $\chi < 0.5$ . When the mixture is produced from two polymers A and B, Eq. (12-24) can be recast in the form

$$\begin{aligned} \Delta G_m = RTV[\chi_{AB}\varphi_A(1 - \phi_A) + (\phi_A/V_A)\ln\phi_A \\ + (\phi_B/V_B)\ln(1 - \phi_A)] \end{aligned} \quad (5-28)$$

where  $V$  is the total volume of the mixture,  $V_i$  is the molar volume of species  $i$ , and  $\chi_{AB}$  is the interaction parameter for the two polymeric species. Since  $V_i = M_i/\rho_i$  this is also equivalent to

$$\begin{aligned} \Delta G_m = RTV[\chi_{AB}\varphi_A(1 - \phi_A) + (\phi_A\rho_A/M_A)\ln\phi_A \\ + (\phi_B\rho_B/M_B)\ln(1 - \phi_B)] \end{aligned} \quad (5-29)$$

The logarithmic terms are negative because the  $\varphi_i$  are less than one. Therefore,  $\Delta G_m$  is less negative and the mixture is less stable the higher the molecular weights of the components. In fact, mixtures of high polymers are indicated to be always incompatible unless  $\chi_{AB} \leq 0$ . This situation will occur only when the enthalpy of mixing is less than or equal to zero, i.e., when there are some specific interactions (not of the van der Waals type) between the components of the mixture.

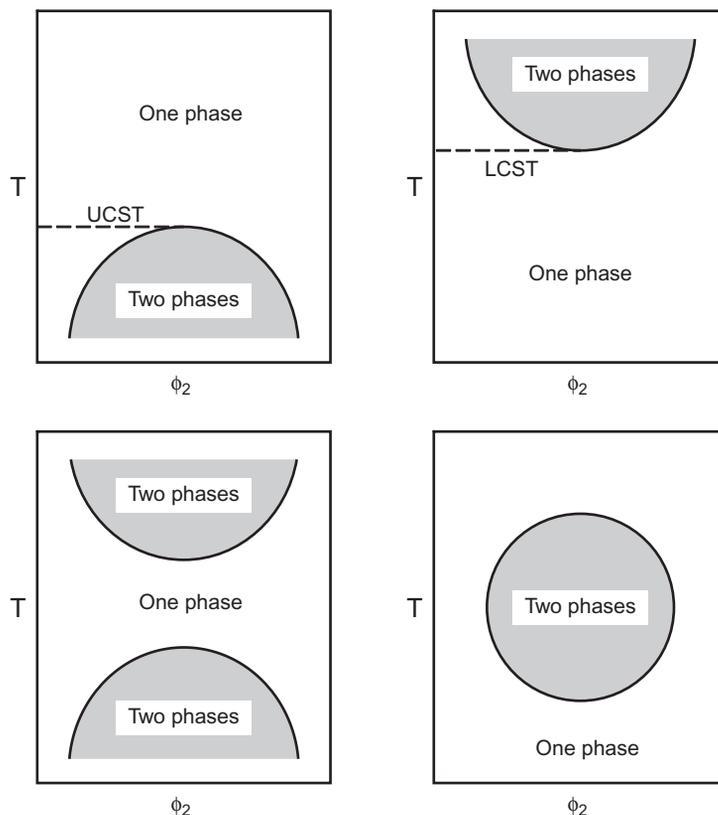
The Flory–Huggins theory predicts that the solubility of polymers will be inversely related to their molecular sizes. Compatibility of polymers with other materials is certainly affected by the molecular weight of the macromolecules. Higher molecular weight materials are generally less soluble in solvents. The influence of molecular weight on the stability of other mixtures is more complex. Higher molecular weight species are generally more difficult to disperse, especially if they are minor components of mixtures in which the major species are lower molecular weight, less viscous substances. If they can be dispersed adequately, however, their diffusion rates and consequent rates of segregation will be correspondingly less and the dispersion may appear to be stable as a result.

The Flory–Huggins model differs from the regular solution model in the inclusion of a nonideal entropy term due to the difference in the sizes of molecules of different kinds and replacement of the enthalpy term in solubility parameters by

one in an interaction parameter  $\chi$ . This parameter characterizes a *pair* of components whereas each  $\delta$  can be deduced from the properties of a single component.

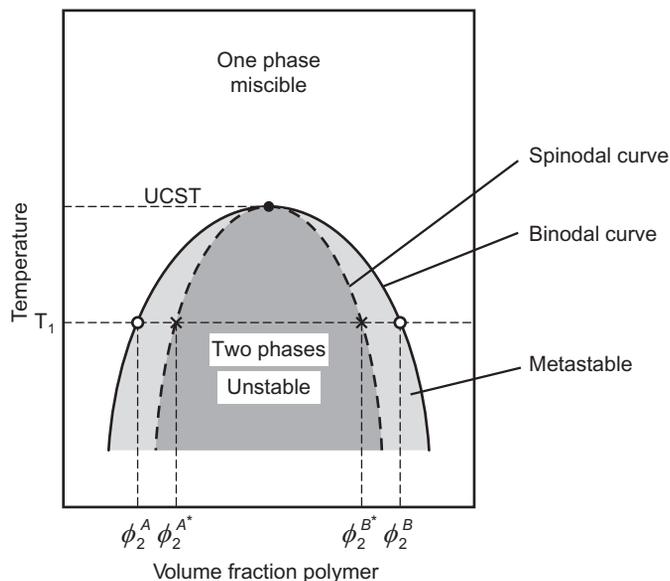
In the initial theory,  $\chi$  was taken to be a function only of the nature of the components in a binary mixture. It became apparent, however, that it depends on concentration and to some extent on molecular weight. It is now considered to be a free energy of interaction and thus consists of enthalpic and entropic components with the latter accounting for its temperature dependence.

The Flory–Huggins theory does not predict the lower critical solution temperature (LCST) phase behavior in which the components phase separate at high temperatures but are miscible at low temperatures. As mentioned, most miscible polymer solutions and blends require favorable specific interactions (e.g., hydrogen bonds). And such interactions will diminish as temperature is increased, leading to phase separation. Figure 5.2 schematically illustrates the possible phase behavior of polymer solutions and blends. The reason that the Flory–Huggins theory is not



**FIGURE 5.2**

Schematic representation of various phase diagrams of polymer solutions and blends.

**FIGURE 5.3**

Schematic representation of spinodal and binodal curves.

able to predict the upper critical solution temperature (UCST) phase behavior is that  $\chi$  decreases with increasing temperature (Eq. 5-20). Using a UCST mixture as an example, Fig. 5.3 shows that within the immiscible region, there exist unstable and metastable regions. They are bounded by the spinodal and binodal curves that meet at the critical temperature. At the critical temperature, the partial second and third derivatives of the chemical potentials of the components are zero. This leads to the following equation for the determination of critical  $\chi$ .

$$\chi_{\text{critical}} = \frac{1}{2} \left( \frac{1}{\sqrt{r_1}} + \frac{1}{\sqrt{r_2}} \right)^2 \quad (5-30)$$

For a mixture that contains two types of small molecules with comparable sizes,  $r_1 = r_2 = 1$ ,  $\chi_{\text{critical}} = 2$  (regular solution theory). For a mixture that contains a solvent and a polymer,  $r_1 = 1$  and  $r_2$  tends to be large,  $\chi_{\text{critical}} = 0.5$ . When both components in a mixture are polymers,  $\chi_{\text{critical}} = 0$ . Here, mixtures that exhibit  $\chi$  values above  $\chi_{\text{critical}}$  would phase separate.

### EXAMPLE 5-1

A blend consists of 40 vol% PE and 60 vol% PS. The degrees of polymerization, based on the molar volume of ethylene, are 1000. At 300 K, the molar volumes of the repeating units of PE and PS are 32.74 cm<sup>3</sup>/mol and 84.16 cm<sup>3</sup>/mol, respectively. From small angle reaction scattering experiments,  $\chi$  was measured to be 0.10 at 300 K.

- (a) Calculate the actual DP of PE and PS.  
 (b) Calculate  $\Delta S_m$ ,  $\Delta H_m$ , and  $\Delta G_m$ .  
 (c) Calculate  $\chi_{\text{critical}}$ .

**Solution**

- (a) PE:  $32.74 \text{ cm}^3/\text{mol} \rightarrow \text{DPPE} = 1000$

PS:  
 $84.16 \text{ cm}^3/\text{mol} \rightarrow \text{each unit occupies } \frac{84.16}{32.74} = 2.57 \text{ lattice sites. } \therefore \text{DP}_{\text{PS}} = \frac{1000}{2.57} = 389$

- (b)

$$\Delta S_m = -R \left( \frac{0.4}{1000} \ln 0.4 + \frac{0.6}{1000} \ln 0.6 \right)$$

$$= 0.0056 \text{ J/mol}\cdot\text{K}$$

$$\Delta H_m = \chi RT \phi_1 \phi_2$$

$$= 0.1 \times 8.314 \times 300 \times 0.4 \times 0.6$$

$$= 59.86 \text{ J/mol}$$

$$\Delta G_m = 59.86 - 300(0.0056) = 58.2 \text{ J/mol}$$

(c) 
$$\chi_{\text{critical}} = \frac{1}{2} \left( \frac{1}{\sqrt{1000}} + \frac{1}{\sqrt{1000}} \right)^2 = 0.002$$

**EXAMPLE 5-2**

According to the Flory–Huggins lattice theory, the activity coefficient of a solvent (i.e.,  $\gamma_1$ ) in a solvent (1)-polymer (2) mixture is given by the following equation:

$$\ln \gamma_1 = \ln \frac{\phi_1}{x_1} + \left( 1 - \frac{1}{m} \right) (1 - \phi_1) + \chi (1 - \phi_1)^2$$

- (a) For a solvent at infinite dilution in a polymer with infinite molecular weight, show that  $\chi$  is given by the following equation:

$$\chi = \ln \gamma_1 - \left( 1 + \ln \frac{\phi_1}{x_1} \right)$$

- (b) Both  $\phi_1$  and  $x_1$  for a particular solvent-polymer system are measured to be 0.001 and 0.02, respectively; if the interaction energy of the components in this system follows the geometric mean rule (i.e.,  $\chi$  can be calculated using the individual components' Hildebrand solubility parameters), show that the minimum possible  $\gamma_1$  for such a system is 0.135.  
 (c) At  $100^\circ\text{C}$ ,  $\gamma_1$  and the reference volume based upon which  $\chi$  is calculated are determined to be 0.2 and  $55 \text{ cm}^3/\text{mol}$ , respectively; calculate the difference in the solubility parameters of the solvent and polymer  $(\text{cal}/\text{cm}^3)^{1/2}$ .  $R = 1.987 \text{ cal}/\text{mol}\cdot\text{K}$ .

**Solution**

- (a) 
$$\ln \gamma_1 = \ln \frac{\phi_1}{x_1} + \left( 1 - \frac{1}{m} \right) (1 - \phi_1) + \chi (1 - \phi_1)^2$$
  
 Infinite dilution  $\rightarrow \phi_1 \sim 0$   
 Infinite molecular weight  $\rightarrow 1/m \rightarrow 0$

$$\ln \gamma_1 = \ln \frac{\phi_1}{x_1} + 1 + \chi$$

$$\begin{aligned}\chi &= \ln \gamma_1 - 1 - \ln \frac{\phi_1}{x_1} \\ &= \ln \gamma_1 - \left( 1 + \ln \frac{\phi_1}{x_1} \right)\end{aligned}$$

(b) Geometric mean assumption  $\rightarrow$  i.e.,  $\chi \geq 0$ .

$$0 = \ln \gamma_1 - \left( 1 + \ln \frac{\phi_1}{x_1} \right)$$

$$\ln \gamma_1 = 1 + \ln \left( \frac{0.001}{0.02} \right)$$

$$\ln \gamma_1 = -2.0$$

$$\gamma_1 = 0.135$$

(c)

$$\chi = \ln(0.2) - \left( 1 + \ln \frac{0.001}{0.02} \right) = 0.39$$

$$0.39 = \frac{55}{(1.987)(373)} (\delta_s - \delta_p)^2$$

$$(\delta_s - \delta_p) = 2.3 \text{ (cal/cm}^3\text{)}^{1/2}$$

The Flory–Huggins theory has been modified and improved and other models for polymer solution behavior have been presented. Many of these theories are more satisfying intellectually than the solubility parameter model but the latter is still the simplest model for predictive uses. The following discussion will therefore focus mainly on solubility parameter concepts.

### 5.2.3 Modified Solubility Parameter Models

The great advantage of the solubility parameter model is in its simplicity, convenience, and predictive ability. The stability of polymer mixtures can be predicted from knowledge of the solubility parameters and hydrogen-bonding tendencies of the components. The predictions are not always very accurate, however, because the model is so oversimplified. Some examples have been given in the preceding section. More sophisticated solution theories are not predictive. They contain parameters that can only be determined by analysis of particular mixtures, and it

is not possible to characterize individual components *a priori*. The solubility parameter scheme is therefore the model that is most often applied in practice.

Numerous attempts have been made to improve the predictive ability of the solubility parameter method without making its use very much more cumbersome. These generally proceed on the recognition that intermolecular forces can involve dispersion, dipole–dipole, dipole-induced dipole, or acid–base interactions, and a simple  $\delta$  value is too crude an overall measurement of these specific interactions.

The most comprehensive approach has been that of Hansen [10,11], in which the cohesive energy  $\delta^2$  is divided into three parts:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_H^2 \quad (5-31)$$

where the subscripts d, p, and H refer, respectively, to the contributions due to dispersion forces, polar forces, and hydrogen-bonding. A method was developed for the determination of these three parameters for a large number of solvents. The value of  $\delta_d$  was taken to be equal to that of a nonpolar substance with nearly the same chemical structure as a particular solvent. Each solvent was assigned a point in  $\delta_d, \delta_p, \delta_H$  space in which these three parameters were plotted on mutually perpendicular axes. The solubility of a number of polymers was measured in a series of solvents, and the  $\delta_p$  and  $\delta_H$  values for the various solvents which all dissolved a given polymer were shifted until the points for these solvents were close. This is a very tedious and inexact technique. More efficient methods include molecular dynamics calculations [12] and inverse gas chromatographic analyses [13].

The three-dimensional solubility parameter concept defines the limits of compatibility as a sphere. Values of these parameters for some of the solvents listed earlier in Table 5.3 are given in Table 5.4. More complete lists are available in handbooks and technological encyclopedias. The recommended procedure in conducting a solubility parameter study is to try to dissolve the polymeric solute in a limited number of solvents that are chosen to encompass the range of subsolubility parameters. A three-dimensional plot of solubility then reveals a “solubility volume” for the particular polymer in  $\delta_d, \delta_p, \delta_H$  space.

Three-dimensional presentations are cumbersome and it is more convenient to transform the Hansen parameters into fractional parameters as defined by [14]

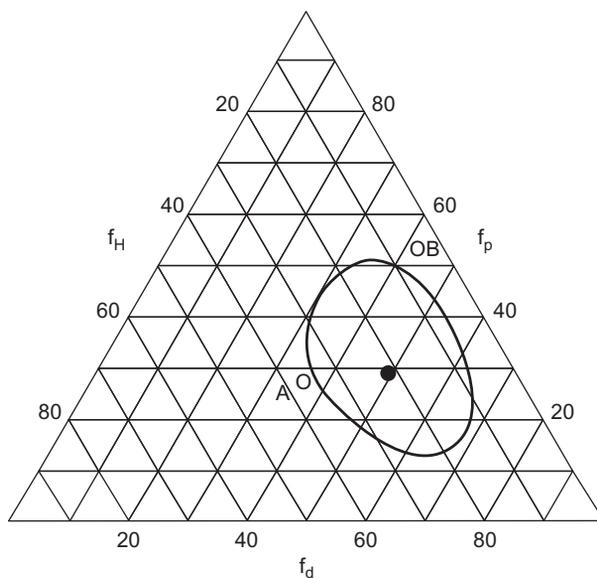
$$f_d = \delta_d/\delta \quad (5-31a)$$

$$f_p = \delta_p/\delta \quad (5-31b)$$

$$f_H = \delta_H/\delta \quad (5-31c)$$

The data can now be represented more conveniently in a triangular diagram, as in Fig. 5.4. This plot shows the approximate limiting solubility boundaries for poly(methyl methacrylate). The boundary region separates efficient from poor solvents. The probable solubility parameters of the solute polymer will be at the heart of the solubility region. The boundaries are often of greater interest than the

	$\delta_d$	$\delta_p$	$\delta_H$
<i>N</i> -Hexane	14.9	0	0
Benzene	18.4	0	0
Chloroform	17.8	3.1	5.7
Nitrobenzene	18.8	12.4	4.1
Diethyl ether	14.7	2.9	5.2
Iso-amyl acetate	15.5	3.1	7.0
Diocetyl phthalate	16.7	7.0	3.1
Methyl isobutyl ketone	15.5	6.2	4.1
Tetrahydrofuran	16.9	5.8	8.1
Methyl ethyl ketone	16.1	9.1	5.2
Acetone	15.7	10.5	7.0
Diethylene glycol monomethyl ether	16.3	7.8	12.8
Dimethyl sulfoxide	18.6	16.5	10.3
Acetic acid	14.7	8.0	13.6
<i>m</i> -Cresol	18.2	5.2	13.0
1-Butanol	16.1	5.8	15.9
Methylene glycol	16.3	14.9	20.7
Methanol	15.3	12.4	22.5

**FIGURE 5.4**

Limiting solubility boundary for poly(methyl methacrylate) [14]. The solid circle represents the solubility parameters of the resin.

central region of such loops because considerations of evaporation rates, costs, and other properties may also influence the choice of solvents.

The design of blended solvents is facilitated by use of these subparameters, along with graphical analyses. Thus, referring again to Fig. 5.4, the polymer will be insoluble in solvents A and B but a mixture of the two should be a solvent. It has been suggested also that a plot of  $\delta_p$  versus  $\delta_H$  should be sufficient for most practical purposes, since  $\delta_d$  values do not vary greatly, at least among common solvents.

The procedures outlined have a practical use, but it should be realized that the subparameter models have some empirical elements. Assumptions such as the geometric mean rule (Eq. 5-6) for estimating interaction energies between unlike molecules may have some validity for dispersion forces but are almost certainly incorrect for dipolar interactions and hydrogen bonds. Experimental uncertainties are also involved since solubility “loops” only indicate the limits of compatibility and always include doubtful observations. Some of the successes and limitations of various versions of the solubility parameter model are mentioned in passing in the following sections which deal briefly with several important polymer mixtures.

---

## 5.3 Solvents and Plasticizers

### 5.3.1 Solvents for Coating Resins

The most widespread use of the solubility parameter has been in the formulation of surface coatings. Single solvents are rarely used because the requirements for evaporation rates, safety, solvency, and so on generally mean that a solvent blend is more effective and less costly. Further, use of nonsolvents is often effective for cost reductions. The cheapest organic solvents are hydrocarbons, whereas most solvents for film-forming polymers are moderately hydrogen bonded and have  $\delta$  values in the range 16–20 (MPa)<sup>1/2</sup>. The simple example that was given in connection with Fig. 5.4 illustrates how such blends can be formulated. The procedure can be used to blend solvents with nonsolvents or even to make a solvent mixture from nonsolvents. The latter procedure must be used with caution for surface coatings, however, since the effective solubility parameter of the system will drift toward those of the higher boiling components as the solvents evaporate. If these residual liquids are nonsolvents the final coalesced polymer film may have poor clarity and adhesion to the substrate. The slowest evaporating component of the solvent blend should be a good solvent for the polymer in its own right, since the last solvent to leave the film has a strong influence on the quality of the film.

### 5.3.2 Plasticization of Polymers

A plasticizer is a material that enhances the processability or flexibility of the polymer with which it is mixed. The plasticizer may be a liquid or solid or

another low-molecular-weight polymer. For example, rigid poly(vinyl chloride) is a hard solid material used to make credit cards, pipe, house siding, and other articles. Mixing with about 50–100 parts by weight of phthalate ester plasticizers converts the polymer into leathery products useful for the manufacture of upholstery, electrical insulation, and other items. Plasticizers in surface coatings enhance the flow and leveling properties of the material during application and reduce the brittleness of the dried film.

Some degree of solvency of the plasticizer for the host polymer is essential for plasticization. Not surprisingly, a match of solubility parameters of the plasticizer and polymer is often a necessary but not a sufficient condition for compatibility. In the case of PVC, the dielectric constants of the plasticizer should also be near that of the polymer.

It is often useful to employ so-called “secondary plasticizers,” which have limited compatibility with the host polymer. Thus, aliphatic diesters are poorly compatible with PVC, but they can be combined with the highly compatible phthalate ester plasticizers to improve low-temperature properties of the blend.

Continued addition of a plasticizer to a polymer results in a progressive reduction in the glass transition temperature of the mixture. This suggests that the plasticizer acts to facilitate relative movement of macromolecules. This can happen if the plasticizer molecules are inserted between polymer segments to space these segments farther apart and thus reduce the intensity of polymer–polymer interactions. Such a mode of action is probably characteristic of low-temperature plasticizers for PVC, like dioctyl adipate. Plasticizers with more specific interactions with the polymer will reduce the effective number of polymer–polymer contacts by selectively solvating the polymer at these contact points. PVC plasticizers like diisooctyl phthalate seem to act in the latter fashion.

Rubbers are plasticized with petroleum oils, before vulcanization, to improve processability and adhesion of rubber layers to each other and to reduce the cost and increase the softness of the final product. Large quantities of these “oil-extended” rubbers are used in tire compounds and related products. The oil content is frequently about 50 wt% of the styrene–butadiene rubber. The chemical composition of the extender oil is important. Saturated hydrocarbons have limited compatibility with most rubbers and may “sweat-out.” Aromatic oils are more compatible and unsaturated straight chain and cyclic compounds are intermediate in solvent power.

---

## 5.4 Fractionation

The properties of a polymer sample of given composition, structure, and average molecular weight are not uniquely determined unless the distribution of molecular weight about the mean is also known. Methods to determine this distribution include gel permeation (size exclusion) chromatography and various fractionation techniques. Fractionation is a process for the separation of a chemically

homogeneous polymer specimen into components (called “fractions”) which differ in molecular size and have narrower molecular-weight distributions than the parent material. Ideally, each fraction would be monodisperse in molecular weight but such a separation has not been approached in practice and the various fractions that are collected always overlap to some extent.

It should be noted that all the fractionation process does is provide narrower molecular weight distribution materials. The molecular weight distribution of the original material cannot be reconstructed until the average molecular weight of each fraction is obtained by other independent measurements.

Fractionation depends on the differential solubility of macromolecules with different sizes. It has been displaced in many cases by size exclusion chromatography as a means for measuring molecular weight distributions, but it is still often the only practical way of obtaining narrow fractions in sufficient quantities for the study of physical properties of well-characterized specimens. It is also part of the original procedure for the calibration of solution viscosity measurements for the estimation of molecular weights.

The Flory–Huggins theory leads to some useful rules for fractionation operations. Only the results will be summarized here. Details of the theory and experimental methods are available in Refs. [15,16] and other sources.

Consider a polymeric species with degree of polymerization  $i$  in solution. The homogeneous solution can be caused to separate into two phases by decreasing the affinity of the solvent for the polymer by lowering the temperature or adding some poorer solvent, for example. If this is done carefully, a small quantity of polymer-rich phase will separate and will be in equilibrium with a larger volume of a solvent-rich phase. The chemical potential of the  $i$ -mer will be the same in both phases at equilibrium, and the relevant Flory–Huggins expression is

$$\ln(\phi'_i/\phi_i) = \sigma_i \quad (5-32)$$

where  $\phi'_i$  and  $\phi_i$  are the volume fraction of polymer of degree of polymerization  $i$  in the polymer-rich and solvent-rich phases, respectively. Sigma ( $\sigma$ ) is a function of the volume fractions mentioned and the number average molecular weights of all the polymers in each phase, as well as the dimensionless parameter  $\chi$  (Eq. 5-23). Sigma cannot be calculated exactly, but it can be shown to be always positive [15]. It follows then from Eq. (5-32) that  $\phi'_i > \phi_i$ , regardless of  $i$ . This means that all polymer species tend to concentrate preferentially in the polymer-rich phase. However, since  $\phi'_i/\phi_i$  increases exponentially with  $i$ , the latter phase will be relatively richer in the larger than in the smaller macromolecules.

Fractionation involves the adjustment of the solution conditions so that two liquid phases are in equilibrium, removal of one phase and then adjusting solution conditions to obtain a second separated phase, and so on. Polymer is removed from each separated phase and its average molecular weight is determined by some direct measurement such as osmometry or light scattering.

It is evident that both phases will contain polymer molecules of all sizes. The successive fractions will differ in average molecular weights but their

distributions will overlap. Various mathematical techniques have been used to allow for such overlapping in the reconstruction of the molecular weight distribution of the parent polymer from the average molecular weights measured with fractions.

Although refractionation may narrow the molecular weight distributions of “primary” fractions, such operations are subject to a law of diminishing returns because of the complications of Eq. (5-32) that have just been mentioned.

If the volumes of the polymer-rich and solvent-rich phases are  $V'$  and  $V$ , respectively, then the fraction  $f_i$  of  $i$ -mer that remains in the solvent-rich phases is given by

$$f_i = \frac{\phi_i V}{\phi_i V + \phi_i' V'} = \frac{1}{1 + \text{Re}^{\sigma_i}} \quad (5-33)$$

where  $R = V'/V$ . Similarly, the fraction of  $i$ -mer in the polymer-rich phase is

$$f_i' = \text{Re}^{\sigma_i} / (1 + \text{Re}^{\sigma_i}) \quad (5-34)$$

and

$$f_i/f_i' = 1/\text{Re}^{\sigma_i} \quad (5-35)$$

If the volume of the solvent-rich phase is much greater than that of the polymer-rich phase ( $R \ll 1$ ), then most of the smaller macromolecules will remain in the former phase (Eq. 5-35). Also, as  $i$  increases, the proportion of  $i$ -mer in the polymer-rich phase will increase.

Dilute solutions are needed for efficient fractionation. When fractionation is effected by gradual precipitation of polymer from solution, good practice requires that the initial polymer concentration decrease with increasing molecular weight of the whole polymer. A 10-g sample of a low-molecular-weight polymer should be dissolved in about 1 liter of solvent while a high-molecular-weight polymer might easily require 10 liters.

Temperature rising elution fractionation (TREF) is a useful technique for characterizing the distribution of branches and other uncrystallizable entities in semi-crystalline polymers. Recall that regularity of polymer structure is necessary for crystallizability (Section 1.11.2) and branches and comonomer residues cannot usually fit into crystal lattices. This method is particularly valuable with polyolefins like polyethylene, whose properties are affected by the distributions of both molecular weight and branching [17]. The procedure involves dissolution of the sample in a solvent, followed by slow cooling to deposit successive layers of less and less crystallizable species onto an inert substrate, like silanized silica. The material here consists of onion-skin layers of polymer, with the least regular (i.e., most branched) species on the outside. The foregoing procedure is then reversed, as the precipitated polymer is eluted by flowing solvent at progressively increasing temperatures. The concentration of eluting dissolved polymer and the corresponding branch concentration can be monitored by infra-red detection at different wavelengths [18].

---

## 5.5 Practical Aspects of Polymer Blending [19]

Polymer blends have become a very important subject for scientific investigation in recent years because of their growing commercial acceptance. Copolymerization and blending are alternative routes for modifications of properties of polymers. Blending is the less expensive method. It does not always provide a satisfactory alternative to copolymerization, of course, but polymer blends have been successfully used in an increasing number of applications in recent years. Such successes encourage more attempts to apply this technique to a wider range of problems in polymer-related industries.

### 5.5.1 Objectives in Making Blends

It is usually, but not always, desired to make a blend whose properties will not change significantly during its normal usage period. Unstable blends are sometimes required, however. An example is the use of slip agents (surface lubricants) in polyolefin films. The additives must be sufficiently compatible with the host resin not to exude from the polymer melt onto the extruder barrel walls during film extrusion. If the slip agent migrated to this boundary the resin would turn with the screw and would not be extrudable. The slip agent must exude from the solid polymer, however, since its lubrication function is exercised only on the surface of the final film. Amides of long chain fatty acids have the right balance of controlled immiscibility for such applications in polyolefin plastics. Lubricants and antistatic agents are other examples of components of blends that are not designed to be stable.

This section will concentrate on stable blends since these are of greater general interest. It should be noted that stability in this context does not necessarily imply miscibility or even that the mixture attains a state of thermodynamic equilibrium during its useful lifetime. More generally, all that is required is that the components of the mixture adhere to each other well enough to maintain an adequate mechanical integrity for the particular application and that this capacity be maintained for the expected reasonable lifetime of the particular article.

### 5.5.2 Blending Operations

The manufacture of useful, stable blends involves two major steps: (1) The components are mixed to a degree of dispersion that is appropriate for the particular purpose for which the blend is intended; (2) additional procedures are followed, if necessary, to ensure that the dispersion produced in step 1 will not demix during its use period.

Note that it is useful to consider step 2 as a problem involving retardation of a kinetic process (demixing). The viewpoint that focuses on blending as a problem in thermodynamic stability is included here as a special case but should not

exclude other routes to stabilization which may be practical under some circumstances.

To illustrate this point consider the production of lacquers for PVC films and sheeting. Such lacquers contain a PVC homopolymer or low-acetate vinyl chloride-vinyl acetate copolymer, poly(methyl methacrylate), a plasticizer and perhaps some stabilizers, dulling agents (such as silica), pigments, and so on. Methyl ethyl ketone (MEK) is the solvent of choice because it gives the best balance of low toxicity, volatility, and cost. Any other solvent is effectively excluded for a variety of reasons such as cost, inadequate volatility for coating machines designed to dry MEK, unfamiliar odor, toxicity, and so on. Unfortunately, MEK is really a poor solvent for this mixture. The solids concentrations required for effective coatings result in a mucuslike consistency if the lacquer is produced by conventional slow speed stirring and heating. The mixture is very thixotropic and tends to form uneven coatings and streaks when applied by the usual roller coating methods. For reasons listed above the addition of better solvents is not an acceptable route to improvement of the quality of the coating mixture.

A practical procedure is readily apparent, however, if one proceeds by steps 1 and 2 above. A good dispersion is first made by intensive mechanical shearing. High energy mixers are available which can boil the solvent in a few minutes just from the input of mechanical work. The solid ingredients are added slowly to the initially cold solvent while it is being sheared in such an apparatus. This produces a finely dispersed, hot mixture. It is not a true solution, however, and will revert eventually to a mucuslike state. To retard this demixing process one can add a small concentration of an inexpensive nonsolvent like toluene. This makes the liquid environment less hospitable for the solvated polymer coils which shrink and are thus less likely to overlap and segregate. The final mixture is still not stable indefinitely, but it can be easily redispersed by whipping with an air mixer at the coating machine.

Although the scientific principles behind this simple example of practical technology are easily understood, it illustrates the benefits that can be realized by considering the blending process as a dispersion operation that may be followed, if necessary, by an operation to retard the rate at which the ingredients of the blend demix. In special cases, of course, the latter operation may be rendered unnecessary by the selection of blend ingredients that are miscible in the first instance.

The basic requirements for achieving good dispersions of polymeric mixtures have been reviewed elsewhere [21–23] and will not be repeated here in any detail. Extruders and intensive mixers produce mainly laminar mixing in which the interfacial area between components of the mixture is increased in proportion to the total amount of shear strain which is imparted to the fluid substrate. Better laminar mixing is realized if the viscosities of the components of the blend are reasonably well matched. Such mixers operate by moving their inner metal surfaces relative to each other. Shear strain is imparted to the polymer mixture if it adheres to the moving walls of the mixer. When the ingredients of the mixture

have different viscosities, the more fluid component will take up most or all of the imparted strain, particularly if it is the major ingredient of the mixture. Thus it is easy to melt blend a minor fluid component with a major, more viscous ingredient, but a minor viscous component may swim in a more fluid sea of the major component without being dispersed. Similar considerations apply if there are serious mismatches in the melt elasticities of the components of a mixture.

It is also well known in compounding technology that the quality of a dispersion may be sensitive to the condition of the blend that is fed to the mixing machine and in some cases also to the order in which the ingredients are added to the mixer.

Some mixers provide dispersive as well as laminar mixing. In dispersive mixing, the volume elements of the compound are separated and shuffled. Dispersive mixing processes can be added to laminar mixing operations by introducing mixing sections into extruder screws or installing stationary mixers in the extruder discharge sections.

The correlation between quality of a laminar mixture and the total shear strain that the material has undergone applies particularly to blends of polymers. When hard or agglomerated components are being mixed, however, it is necessary to subject such materials to a high shear stress gradient, and special equipment and processes have been developed for such purposes. The rubber and coatings industries in particular abound with examples of such techniques.

Special note should be taken of the difficulty of forming intimate mixtures of some semicrystalline polymers, and particularly of polyethylenes. Experimental and theoretical studies have shown that local structure persists in such polymers even at temperatures above the  $T_m$  measured by differential scanning calorimetry (DSC). These structures consist of folded chain domains in polyethylenes and of helical entities in polypropylene. That is to say, in these polymers, at least, the lowest energy states of the uncrystallized material are characterized by minima in free energy, rather maxima in entropy. Molecular dynamics simulations of mixtures of linear polyethylene and isotactic polypropylene indicate that the two species will segregate into distinct domains in the melt even when the initial state was highly interpenetrating [24]. Such domains also form in the mixtures of polyethylenes with different branching characteristics [25,26]. The formation of locally ordered regions is expected to be more significant for longer polymer chains. From a theoretical point of view, such observations imply that the mixing of polymers cannot be described adequately by a purely statistical model as in the original Flory–Huggins formulation. This theory has been generalized by some researchers to decompose the interaction parameter,  $\chi$ , into enthalpic and entropic terms, where the latter may be construed as reflecting “local structures” [27].

Practically, the foregoing phenomena indicate the difficulty, or perhaps the impossibility, of forming molecular level mixtures of polyethylenes with other polymers, or with other polyethylenes, by conventional techniques which operate on polymers in which some local order has already been established during polymerization. In a sense, then, “polyethylene is not compatible with polyethylene.”

as can be seen in the persistence of separate DSC melting patterns after intensive melt mixing of relatively branched and unbranched versions of this polymer.

It is assumed in what follows that a satisfactory dispersion can be obtained despite the problems that may be encountered in special cases, described above. We consider the various procedures that may retard or eliminate the demixing of such dispersions in the following section.

### 5.5.3 Procedures to Retard or Eliminate Demixing of Polymer Mixtures

The various procedures that will be discussed are listed in [Table 5.5](#) in order to present an overview of the basic ideas. Each heading in this table is considered briefly in this section.

#### 5.5.3.1 Use of Miscible Components

Thermodynamically stable mixtures will of course form stable blends. This implies miscibility on a molecular level. It is desirable for some applications but not for others, like rubber modification of glassy polymers.

1. A particular polymer mixture can be made more miscible by reducing the molecular weights of the components. From [Eq. \(5-1\)](#) any measure that increases the entropy of mixing  $\Delta S_m$  will favor a more negative  $\Delta G_m$ . The Flory–Huggins theory shows that the entropy gain on mixing a polymer is inversely related to its number average size. This is observed in practice. Low-molecular-weight polystyrenes and poly(methyl methacrylate) polymers are miscible but the same species with molecular weights around those of commercial molding grades ( $\sim 100,000$ ) are not.

Advantage can be taken of this enhanced stability of blends of low molecular polymers by chain-extending or cross-linking the macromolecules in such mixtures after they have been formed or applied to a substrate. This procedure is the basis of many formulations in the coatings industry.

**Table 5.5** Procedures to Retard or Eliminate Demixing

- |   |   |
|---|---|
| <ol style="list-style-type: none"> <li>1. Use of miscible components (i.e., <math>\Delta G_m = \Delta H_m - T\Delta S_m \leq 0</math>)               <ol style="list-style-type: none"> <li>(a) Low-molecular-weight polymers</li> <li>(b) Specific interactions to produce negative <math>\Delta H_m</math></li> <li>(c) Generally match solubility parameters</li> </ol> </li> <li>3. Prevent segregation               <ol style="list-style-type: none"> <li>(a) Cross-linking</li> <li>(b) Forming interpenetrating networks</li> <li>(c) Mechanical interlocking of components</li> </ol> </li> </ol> | <ol style="list-style-type: none"> <li>2. Rely on slow diffusion rates               <ol style="list-style-type: none"> <li>(a) Mix high-molecular-weight polymers</li> <li>(b) Cocrystallization</li> </ol> </li> <li>4. Use “compatibilizing agents”               <ol style="list-style-type: none"> <li>(a) Statistical copolymers</li> <li>(b) Graft copolymers</li> <li>(c) Block copolymers</li> </ol> </li> </ol> |
|---|---|

2. Many synthetic polymers are essentially nonpolar and do not participate in specific interactions like acid–base reactions, hydrogen-bonding, or dipole–dipole interactions. In that case, intermolecular interactions are of the van der Waals type and  $\Delta H_m$  in Eq. (5-1) is positive. The only contribution to a negative  $\Delta G_m$  then comes from the small  $\Delta S_m$  term.

If specific interactions do occur between the components of a polymer blend, the mixing process will be exothermic ( $\Delta H_m$  negative) and miscibility can be realized. Water-soluble polymers are often miscible with each other, for example, because they participate in hydrogen bonding.

3. The most widely used method for predicting mixture stability relies on the selection of ingredients with matching solubility parameters and hydrogen-bonding tendencies, as outlined earlier. A small or negative Flory–Huggins interaction parameter value is also characteristic of a stable mixture. Predictions of blend stability can be made quickly from tabulations of solubility and Flory–Huggins parameters. Although such calculations are very useful, they cannot be expected to be universally accurate because the solubility parameter model does not take account of polymer molecular weight and the Flory–Huggins parameter may be concentration dependent.

### 5.5.3.2 Reliance on Slow Diffusion Rates

*High-Molecular-Weight Polymers.* A given blend of two or more polymers can be made more stable by decreasing the molecular weights of the components to the level of oligomers, as mentioned above in connection with polymer miscibility. When a particular blend is not sufficiently stable, it can also paradoxically be improved in this regard by increasing the molecular weights of the ingredients.

Since demixing is a diffusional process, it can be reduced to an acceptable level by using higher molecular weight, more viscous polymers. The difficulty of dispersing such materials to a fine level is correspondingly increased, of course, but if this can be achieved the rate of segregation will also be retarded.

*Cocrystallization.* An additional factor that is operable in some cases involves the ability of the ingredients of a mixture to cocrystallize. These components cannot then demix since portions of each are anchored in the ordered regions in which they both participate. This may be particularly useful for hydrocarbon polymers where favorable enthalpies of mixing do not exist.

Copolymers of ethylene, propylene, and unconjugated diene (EPDM) polymers vary in their usefulness as blending agents for polyethylene. It has been shown that EPDMs with relatively high levels of ethylene can cocrystallize with branched polyethylene or high-ethylene-content copolymers of ethylene with vinyl acetate or methyl methacrylate [28]. Such blends are stable and may have particularly good mechanical properties. Ethylene/propylene copolymers can serve as compatibilizing agents for blends of polypropylene and low density polyethylene. Those copolymers which have residual crystallinity because of longer ethylene sequences are preferable to purely amorphous

materials for this application [29]. Cocrystallization is probably also a factor in this case.

### 5.5.3.3 Prevention of Segregation

Once a satisfactory initial dispersion has been produced various operations can be conducted to reduce or eliminate the rate of demixing. These are considered separately below.

*Cross-Linking.* A thermoset system is produced when a polymer is cross-linked under static conditions, as in a compression mold. This is the basis of the production of vulcanized articles or cross-linked polyethylene pipe and wire insulation. If the same polymer is lightly cross-linked while it is being sheared in the molten state, however, it will remain thermoplastic. If it is more heavily cross-linked during this process, the final product may contain significant quantities of gel particles, but the whole mass will still be tractable.

This technique provides a method for incorporating fillers or reinforcing agents into some polymers which ordinarily do not tolerate such additions. A high loading of carbon black cannot normally be put into polyethylene, for example, without serious deterioration of the mechanical properties of that polymer. Various hydrocarbon elastomers will accept high carbon black contents. Such black-loaded rubbers do not normally form stable mixtures with polyethylene, but strong, permanent blends can be made by carrying out simultaneous blending and cross-linking operations in an internal mixer. If conductive carbon black is mixed carefully with a peroxide or other free radical source, rubber, and the polyolefin, this technique can yield semiconductive compositions in hydrocarbon matrices. When the peroxide decomposes it produces radicals that can abstract atoms from the main chains of polymers. When the resulting macroradicals combine, the parent polymers are linked by primary valence bonds.

The potential exists for chemical bonding of the two polymeric species in such operations but it is not certain that this is always what happens. It is possible in some instances that the stability of the mixture derives mainly from the entanglement of one polymer in a loose, cross-linked network of the other.

The “dynamic cross-linking” process is used to produce thermoplastic elastomers from mixtures of crystallizable polyolefins and various rubbers. Variations of basically the same method are employed to produce novel, stable polymer alloys by performing chemical reactions during extrusion of such mixtures. In that case, the current industrial term is *reactive extrusion*. Such processes are used, for example, to improve processability of LLDPE’s into tubular film (by introducing long chain branches during extrusion with low levels of peroxides) or to modify the molecular weight distribution of polypropylenes (again by extrusion with radical-generating peroxides).

*Interpenetrating Networks.* Interpenetrating networks (IPNs) and related materials are formed by swelling a cross-linked polymer with a monomer and polymerizing and cross-linking the latter to produce interlocked networks. In semi-interpenetrating systems, only the first polymer is cross-linked. Most of

these materials reveal phase separation but the phases vary in size, shape, and sharpness of boundaries depending on the basic miscibility of the component polymers, the cross-link density in the two polymers, and the polymerization method. Some affinity of the components is needed for ordinary interpenetrating networks because they must form solutions or swollen networks during synthesis. This may not be required for IPNs based on latex polymers, where the second stage monomer is often soluble in the first, cross-linked latex polymer.

Blends of elastomers are routinely used to improve processability of unvulcanized rubbers and mechanical properties of vulcanizates like automobile tires. Thus, *cis*-1,4-polybutadiene improves the wear resistance of natural rubber or SBR tire treads. Such blends consist of micron-sized domains. Blending is facilitated if the elastomers have similar solubility parameters and viscosities. If the vulcanizing formulation cures all components at about the same rate the cross-linked networks will be interpenetrated. Many phenolic-based adhesives are blends with other polymers. The phenolic resins grow in molecular weight and cross-link, and may react with the other polymers if these have the appropriate functionalities. As a result, the cured adhesive is likely to contain interpenetrating networks.

*Mechanical Interlocking of Components.* In some instances the polymers in a blend may be prevented from demixing because of numerous mutual entanglements produced by mechanical processing or the polymerization history of the blend.

If the melt viscosities of polypropylene and poly(ethylene terephthalate) polymers are reasonably matched under extrusion conditions, a finely dispersed blend may be produced in fiber form. Orientation of such fibers yields strong filaments in which microfibrils of the two partially crystallized polymers are intertwined and unable to separate. Similar fibers with a sheath of one polymer surrounding a core of the other have no mechanical integrity [30].

Enhanced hydrophilicity or dyeability can be conferred on some acrylonitrile-based polymers by polymerizing them in aqueous media containing polyacrylamide. In this case, also, two separate phases exist but the zones of each component are too highly interpenetrating to permit macro separation and loss of mechanical strength.

Thermoplastic polyolefins (TPOs) are based on blends of polypropylene with ethylene-propylene rubbers. Many perform well as hose, exterior automotive trim, and bumpers without chemical linking of the main polymeric components.

#### **5.5.3.4 Use of “Compatibilizing Agents” [20]**

Mixtures of immiscible polymers can be made more stable by the addition of another material that adheres strongly to the original components of the blend.

Plasticizers perform this function if a single plasticizer solvates the dissimilar major components of a blend. Phthalate esters help to stabilize mixtures of poly(vinyl chloride) and poly(methyl methacrylate), for example. These materials are also plasticizers for polystyrene, and stable blends of this polymer with poly(vinyl

chloride) can be made by adding dioctyl phthalate to a blend of polystyrene and rigid PVC.

The most generally useful compatibilizing agents are copolymers in which each different monomer or segment adheres better to one or other of the blend ingredients. Applications of copolymers are classified here according to structure as statistical, block, or graft copolymers. This seems to be as useful a framework as any within which to organize the review, but it has no fundamental bearing on the properties of blends, and different copolymer types may very well be used in similar applications in polymer mixtures.

It is interesting that a mixture of poly-A and poly-B can sometimes be stabilized by addition of a copolymer of C and D, where A, B, C, and D are different monomers. This occurs if the intermolecular repulsion of C and D units is strong enough that each of these monomer residues is more compatible with one or other of the homopolymer ingredients than with the comonomer to which it is linked chemically.

*Statistical Copolymers.* The term *statistical* is used here to refer to copolymers in which the sequence distribution of comonomers can be inferred statistically from the simple copolymer model (Chapter 9) or alternative theory. In the present context “statistical copolymers” excludes block and graft structures and incorporates all other copolymers. It is useful first of all in this section to point out that statistical copolymers are not mutually miscible if the mixture involves abrupt changes in copolymer composition. Coatings chemists observe this phase separation as haze (internal reflections) in films.

Note also that although a conventional high conversion vinyl copolymer may exhibit a wide range of compositions (depending on the reactivity ratios of the comonomers and the monomer feed composition), there are generally so many mutually miscible intermediate compositions that the extremes can be expected to blend well with the rest of the mixture.

Use of statistical copolymers in blends is usually predicated on the existence of a specific interaction between one of the comonomers in the copolymer and other ingredients in the mixture. Thus PVC is miscible with the ethylene/ethyl acrylate/carbon monoxide copolymers [31]. The homogenizing effect here is a weak acid–base interaction between the carbonyl of the copolymer and the weakly acidic hydrogen atoms attached to the chlorine carrying carbons of the PVC. Ethylene/vinyl acetate/carbon monoxide copolymers are more miscible with PVC, and ethylene/vinyl acetate/sulfur dioxide copolymers are miscible with the same polymer over a very wide composition range.

The morphology and stability of mixtures of PVC with copolymers depend on the composition and mixing history of the blend as well as on the nature of the copolymer. Ethylene/vinyl acetate copolymer is reported to behave essentially as a lubricant between PVC particles at low copolymer concentrations and to begin to form single-phase compositions with PVC with increasing copolymer content in the blend. This situation changes with increasing vinyl acetate content in the copolymer and increasing mixing temperatures, both of which increase the solubility of the copolymer in PVC.

In the coextrusion and lamination of polymers the individual layers are sometimes inherently nonadhering. An expedient to improve the strength of such multi-layer structures involves the use of intermediate “glue” layers between surfaces that do not adhere well. Copolymers are often useful in such glue layers, particularly when the copolymer contains a comonomer that adheres well to one of the surfaces and a comonomer that interacts or is miscible with the other polymer to be bonded. Acid-containing copolymers are often prepared for this purpose. *Ionomers* consisting of partially neutralized ethylene/methyl methacrylate copolymers have been employed to bond polyethylene with nylons and poly(butylene terephthalate). In this case the acid component of the copolymer is capable of hydrogen-bonding interactions with the nylon or polyester. There is also the potential for some interchange between functional groups in the two polymers during melt processing.

*Graft Copolymers.* Graft copolymers themselves may exhibit a two-phase morphology and this influences their behavior in blends. The morphological structure that is observed depends on the relative volume fractions of the backbone and graft polymers and their mutual affinity. If separation occurs it will be on a microphase scale because of the chemical linkages between the two polymer types. Amorphous graft copolymers often have good transparency (if there is no crystalline component) because of the small scale of segregation.

The structure of graft copolymers is generally more complex than that of block polymers in that the trunk polymer may be joined to more than one grafted branch and the nature of the production of such copolymers is such that cross-linking also may occur. For this reason the microphase separation that is observed in graft copolymers alone is less distinct and regular than that seen with block copolymers of the same species.

The component of the graft copolymer that is present in the larger concentration will normally form the continuous phase and exert a strong influence on the physical properties of the unblended material. If both phases are present in nearly equal volume fractions, fabrication conditions will determine which component forms the continuous phase.

Graft copolymers decrease the particle size of the dispersed phase in a binary homopolymer mixture and improve the adhesion of the dispersed and continuous phases. The copolymers accumulate at interfaces because parts of the graft are repelled by the unlike component of the blend. They do not necessarily form optically homogeneous mixtures with homopolymers for this reason.

The major application of graft copolymers is in high-impact polystyrene (HIPS), ABS, and other rubber-toughened glassy polymers. The morphology of such blends depends on their synthesis conditions. They are normally made by polymerizing monomers in which the elastomer is dispersed. The elastomer–monomer mixture will tend to form the continuous phase initially but stirring in the early stages of the polymerization of the glassy polymer produces a phase inversion with a resulting dispersion of monomer-swollen rubber in a polymer/monomer continuous phase. When polymerization is completed, the result is a dispersion of rubbery particles in the rigid matrix.

Requirements for rubber toughening of glassy polymers include (1) good adhesion between the elastomer and matrix, (2) cross-linking of the elastomer, and (3) proper size of the rubber inclusions. These topics are reviewed briefly in the order listed:

1. *Rubber-matrix adhesion.* If adhesion between the glassy polymer and elastomer is not good, voids can form at their interfaces and can grow into a crack. The required adhesion is provided by grafting. Affinity between the matrix and rubber is not needed in such cases. Thus, polybutadiene, which has less affinity for polystyrene than styrene-butadiene copolymer, is a better rubbery additive for polystyrene. The butadiene homopolymer has a lower glass transition temperature and remains rubbery at faster crack propagation speeds than the styrene-butadiene copolymer. The inherently poorer adhesion of the polybutadiene and the matrix is masked by the effectiveness of polystyrene-polybutadiene grafts.
2. *Cross-linking of rubber.* A moderate degree of cross-linking in the rubbery phase of the graft copolymer is required to optimize the contribution of the rubbery phase in blends with glassy polymers. Inadequate cross-linking can result in smearing out of the rubbery inclusions during mechanical working of the blend, while excessive cross-linking increases the modulus of the inclusions and reduces their ability to initiate and terminate the growth of crazes.
3. *Particle size.* In general a critical particle size exists for toughening different plastics. The impact strength of the blend decreases markedly if the average particle size is reduced below this critical size. The decrease in impact strength is not as drastic when the particle size increases beyond the optimum value, but larger particles produce poor surfaces on molded and extruded articles and are of no practical use.

*Block Copolymers.* Block and graft copolymers have generally similar effects of collecting at interfaces and stabilizing dispersions of one homopolymer in another. Most graft copolymers are made at present by free radical methods whereas most commercial block copolymers are synthesized by ionic or step growth processes. As a result, the detailed architecture of block copolymers is more accurately known and controlled.

Many block copolymers segregate into two phases in the solid state if the sequence lengths of the blocks are long enough. Segregation is also influenced by the chemical dissimilarity of the components and the crystallizability of either or both components. This two-phase morphology is generally on a microscale with domain diameters of the order of  $10^{-6}$ – $10^{-5}$  cm.

The critical block sizes needed for domain formation are greater than those needed for phase separation in physical mixtures of the corresponding homopolymers. This is because the conformational entropy of parts of molecules in the block domains is not as high as in mixtures, since placement of segments is restricted by the unlike components to which they are linked. Thus, the minimum molecular

weights of polystyrene and *cis*-polybutadiene for domain formation in AB block copolymers of these species are about 5000 and 40,000, respectively [32].

The properties of block copolymers that are most affected by molecular architecture are elastomeric behavior, melt processability, and toughness in the solid state. The effects of such copolymers in polymer blends can obviously also be strongly influenced by the same factors.

When one component of the block polymer is elastomeric, a thermoplastic rubber can be obtained. This occurs only when the block macromolecules include at least two hard ( $T_g >$  usage temperature) blocks. A diblock structure pins only one end of the rubbery segment, and true network structures can therefore not be produced in such AB species. The volume fraction of the hard block must be sufficiently high ( $\geq 20\%$ ) to provide an adequate level of thermally labile cross-linking for good recovery properties. If the volume fraction of hard material is too high, however, the rigid domains may change from spherical, particular regions to an extended form in which elastic recovery is restricted.

A block copolymer is expected to be superior to a graft copolymer in stabilizing dispersions of one polymer in another because there will be fewer conformational restraints to the penetration of each segment type into the homopolymer with which it is compatible. Similarly, diblock copolymers might be more effective than triblock copolymers, for the same reason, although tri- and multiblock copolymers may confer other advantages on the blend because of the different mechanical properties of these copolymers.

Block copolymers serve as blending agents with simple homopolymers as well as stabilizing agents for mixtures of homopolymers. Blends of a homopolymer with an AB-type block copolymer will be weak if the elastomeric segment of the block polymer forms the sole continuous phase or one of the continuous phases. This problem can be circumvented by cross-linking the rubber after the blend is made or by using an ABA block copolymer in which the central segment (B) is rubbery and the terminal, glassy (A) segments serve to pin both ends of the center portions.

When block copolymers are used in rubber mixes there is no particular advantage to a triblock or multiblock species because the final mixture will be vulcanized in any event.

Linear ABA and  $(AB)_n$  block copolymers can form physical networks that persist at temperatures above the glassy regions of the hard segments. Very high melt elasticities and viscosities are therefore sometimes encountered. The accompanying processing problems can often be alleviated by blending with small proportions of appropriate homopolymers. For example, when styrene–butadiene–styrene triblock rubbers are used as thermoplastic elastomers it is common practice to extend the rubbery phase with paraffinic or naphthenic oils to decrease the cost and viscosity of the compound. (Aromatic oils are to be avoided as they will lower the  $T_g$  of the polystyrene zones.) The accompanying decrease in modulus is offset by the addition of polystyrene homopolymer which also reduces elasticity during processing.

While copolymers are generally used in blends to modify the properties of homopolymers or mixtures of homopolymers, the reverse situation also occurs.

This is illustrated by the foregoing example and also by mixtures of poly(phenylene oxide) (1-14) polymers and styrene–butadiene–styrene triblock thermoplastic elastomers. Minor proportions of the block copolymers can be usefully added to the phenylene oxide polymer to improve the impact strength and processability of the latter. This is analogous to the use of polystyrene or HIPS in such applications. It is interesting also that the incorporation of poly(phenylene oxide) elevates the usage temperature of the thermoplastic elastomer by raising the softening point of the hard zones [33].

A number of studies have been conducted to determine the conditions for production of transparent films when an AB block copolymer is mixed with a homopolymer that is chemically similar to one of the blocks and the blend is cast from a common solvent. All agree that the homopolymer is solubilized into the corresponding domain of the block copolymer when the molecular weight of the homopolymer does not exceed that of the same segment in the block polymer. If the molecular weight of the homopolymer is greater than the molecular weights of the appropriate segments in the block polymer, the system will separate into two phases. When high-molecular-weight polystyrene is added to a styrene–butadiene block copolymer with styrene blocks that are shorter than those of the homopolymer, separate loss modulus transitions can be detected for the polystyrene homopolymer zones and the polystyrene domains in the block copolymer [34].

The behavior observed depends also on the morphology of the block polymer. Thus when the block polymer texture consists of inclusions of poly-B in a continuous matrix of poly-A, addition of homopolymer A will result only in its inclusion in the matrix regardless of the molecular weight of the homopolymer. However, the addition of increasing amounts of poly-B can lead to a whole series of morphologies that eventually include separate zones of poly-B.

When a block copolymer is blended with a homopolymer that differs in composition from either block, the usual result is a three-phase structure. Miscibility of the various components is not necessarily desirable. Thus styrene–butadiene–styrene block copolymers are recommended for blending with high density polyethylene to produce mixtures that combine the relative high melting behavior of the polyolefin with the good low temperature properties of the elastomeric midsections of the block polymers.

It is claimed that the toughening of polystyrene by styrene–butadiene diblock copolymers is augmented by melt blending the components in the presence of peroxides. The grafting and cross-linking that occur are an instance of dynamic cross-linking processes described earlier. Rubbery triblock styrene–butadiene–styrene copolymers toughen polystyrene without the need for cross-linking, for reasons mentioned above.

The compounding of styrene–butadiene–styrene triblock polymers with graft polymer high impact polystyrene is also interesting. Blends of polystyrene and the thermoplastic rubber show worthwhile impact strength increases only when the elastomer is present at a volume fraction  $> \sim 25\%$ . But when the thermoplastic rubber is added to high-impact polystyrene, which already has about 25 vol%

rubber, the result is a product with super-high-impact strength. Also, the thermoplastic rubber can be used to carry fire retardants into the mixture without loss of impact strength.

The major current applications of block copolymers in blends involve styrene–diene polymers, but other block polymers are also useful. Siloxane–alkylene ether block copolymers are widely used as surfactants in the manufacture of polyurethane foams, for example.

---

## 5.6 Reinforced Elastomers

The service performance of rubber products can be improved by the addition of fine particle size carbon blacks or silicas. The most important effects are improvements in wear resistance of tire treads and in sidewall resistance to tearing and fatigue cracking. This reinforcement varies with the particle size, surface nature, state of agglomeration and amount of the reinforcing agent and the nature of the elastomer. Carbon blacks normally are effective only with hydrocarbon rubbers. It seems likely that the reinforcement phenomenon relies on the physical adsorption of polymer chains on the solid surface and the ability of the elastomer molecules to slip over the filler surface without actual desorption or creation of voids.

---

## 5.7 Reinforced Plastics

Particulate fillers are used in thermosets and thermoplastics to enhance rigidity and, mainly, to reduce costs. Examples are calcium carbonate in poly(vinyl chloride) and clays in rubber compounds. Fiber reinforcement is more important technically, however, and the main elements of this technology are reviewed briefly here. Fibers are added to plastics materials to increase rigidity, strength, and usage temperatures. Fiber-reinforced plastics are attractive construction materials because they are stiff, strong, and light. The specific stiffness (modulus/density) and specific strength (tensile strength/density) of glass-reinforced epoxy polymers approximate those of aluminum, for example.

Many reinforced thermoplastic articles are fabricated by injection molding. (This is a process in which the polymeric material is softened in a heated cylinder and then injected into a cool mold where the plastic hardens into the shape of the mold. The final part is ejected by opening the mold.) Thermosetting resins that are frequently reinforced are epoxies (p. 11) and unsaturated polyesters, of which more is said below. Glass fibers are the most widely used reinforcing agents, although other fibrous materials, like aromatic polyamides (1-23), confer advantages in special applications.

The improved mechanical properties of reinforced plastics require that the fiber length exceed a certain minimum value. The aspect ratio (length/diameter)

of the fibers should be at least about 100 for the full benefits of reinforcement. This is why particulates like carbon black are reinforcements only for hydrocarbon elastomers but not for plastics generally.

To estimate the degree of reinforcement from parallel continuous fibers assume that the deformations of the fibers and matrix polymer will be identical and equal to that of the specimen when the composite material is stretched in a direction parallel to that of the fibers. The applied stress is shared by the fibers and polymer according to:

$$\sigma_C A_C = \sigma_F A_F + \sigma_P A_P \quad (5-36)$$

where  $\sigma$  is the stress (force/cross-sectional area),  $A$  is the area normal to the fiber axis and the subscripts C, F, and P refer to the composite material, fiber, and polymer, respectively. Since  $\sigma$  is given by

$$\sigma = Y \quad (5-37)$$

[this is Eq. (4-36)] where  $Y$  is the tensile modulus (with the same units as stress) and  $e$  is the nominal strain (increase in length/original length), then Eq. (5-36) is equivalent to:

$$Y_C A_C = Y_F A_F + Y_P A_P \quad (5-38)$$

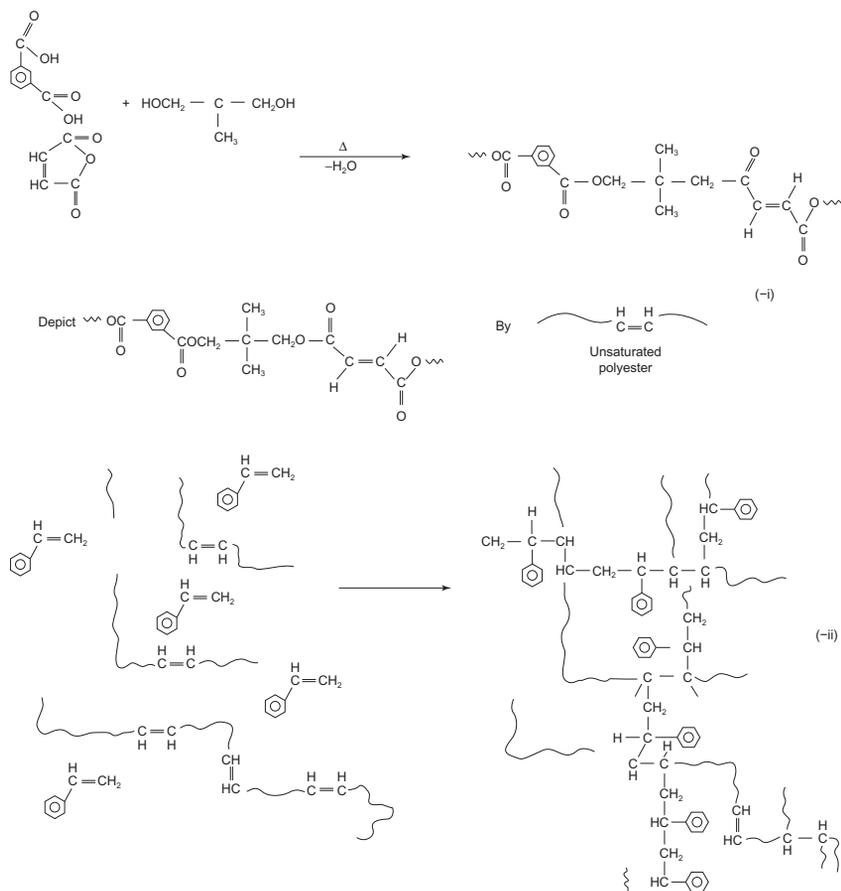
(because  $\epsilon_C = \epsilon_F = \epsilon_P$  in this case). The weight fraction of fiber,  $w_F$ , in the composite is:

$$w_F = \frac{A_F \rho_F}{A_F \rho_F + A_P \rho_P} \quad (5-39)$$

(since the lengths of the specimen, fibers, and polymer component are all equal). Here  $\rho_F$  and  $\rho_P$  are the respective densities of the fiber and polymer. The ratio of the load carried by the polymer to that carried by the fiber is:

$$\frac{\sigma_P A_P}{\sigma_F A_F} = \frac{Y_P A_P}{Y_F A_F} = \frac{Y_P}{Y_F} \cdot \frac{\rho_F}{\rho_P} \left[ \frac{1}{\omega_F} - 1 \right] \quad (5-40)$$

To take a specific example, consider a glass-reinforced polyester laminate, where the chemical reactions involved in polyester technology are sketched in Fig. 5.5. A mixture of saturated and unsaturated acids is mixed with polyhydric alcohols (here shown as a diol) to form an unsaturated polyester. The unsaturated acid (maleic anhydride) provides sites for cross-linkages during subsequent styrene polymerization [shown in reaction (ii)]. Some of the diacid needed to provide sufficient polyester molecular weight ( $\sim 2000$ ) is a saturated species (isophthalic acid in this example) because the cross-linked polymer would be excessively brittle if the cross-links were too close together. The unsaturated polyester produced in step (i) is mixed with a reactive monomer, usually styrene. Glass reinforcement in the proper form is impregnated with the styrene–polyester mixture and “cured” by free-radical polymerization of the styrene across the

**FIGURE 5.5**

Schematic representation of the production of an unsaturated polyester resin and subsequent cross-linking by polymerizing the styrene in a mixture of this monomer with the polyester.

unsaturated linkages in the polyester. Boats and car bodies are among the products made by this process.

In glass-polyester products typical values of the parameters mentioned above are  $Y_F = 70 \text{ GNm}^{-2}$ ,  $Y_P = 3.5 \text{ GNm}^{-2}$ ,  $\rho_F = 2.6 \times 10^3 \text{ kg m}^{-3}$ ,  $\rho_P = 1.15 \times 10^3 \text{ kg m}^{-3}$ , and  $w_F = 0.6$ . Then, from Eq. (5-40), the polymer will bear about 8% of the load taken by the glass fibers. Equation (5-40) is equivalent to:

$$Y_C = \frac{Y_F A_F + Y_P A_P}{A_C} = Y_F \phi_F + Y_P [1 - \phi_F] \quad (5-41)$$

where  $\phi_F$  is the volume fraction of fiber in the composite (since  $\phi_F = A_F/A_C$  for continuous fibers). This is the “law of mixtures” rule for composite properties. With the cited values,  $\phi_F$  in the present example is 0.40 and the modulus of the composite is about 43% of the fiber modulus. The fiber alignment is also a significant factor in composite properties. If the fibers in the foregoing example were randomly oriented their reinforcing effect would be less than 0.2 of the figure calculated above.

Discontinuous fibers are used when the manufacturing process prohibits the application of continuous fibers, for example, in injection molding. In composites of discontinuous fibers, stress cannot be transmitted from the matrix polymer to the fibers across the fiber ends. Under load, the polymer is subjected to a shear stress because the stress along each fiber will be zero at its ends and a maximum,  $\sigma_m$ , at its center. The shear stress at the fiber–polymer interface transmits the applied force between the components of the composite. The shear strength of this interface is typically low and reliance must therefore be placed on having sufficient interfacial area to transmit the load from the polymer to the fiber. This means that the discontinuous fibers must be longer than a certain critical minimum length,  $l_c$ , which depends on the interfacial shear stress,  $\tau$ , fiber diameter, and applied load. Experience shows that this minimum length is not difficult to exceed in dough or sheet molding compounds, where unsaturated polyesters are mixed with chopped fiber mats, with fiber lengths about 5–14 mm. These composites are usually compression molded and cured hot in the mold. The process does not damage the fiber to any significant extent. In injection molding, on the other hand, the initial fibers are likely to be shortened by the mechanical action of the compounding process and the shearing action of the reciprocating screw in the injection molder. They are thus less likely to be effective than in sheet molding formulations.

The properties of fiber–polymer composites are influenced by the strength of the bond between the phases, since stresses must be transmitted across their boundaries. Some problems have been encountered in providing strong interfacial bonds because it is difficult to wet hydrophilic glass surfaces with generally hydrophobic viscous polymers. Coupling agents have therefore been developed to bind the matrix and reinforcing fibers together.

These agents often contain silane or chromium groupings for attachment to glass surfaces, along with organic groups that can react chemically with the polymer. Thus vinyltriethoxysilane [ $\text{H}_2\text{C}=\text{CHSi}(\text{OC}_2\text{H}_5)_3$ ] is used for glass-unsaturated polyester systems and  $\gamma$ -aminopropyltriethoxysilane [ $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$ ] is a coupling agent for glass-reinforced epoxies and nylons. The silanes which seem to couple effectively to glass are those in which some groups can be hydrolyzed to silanols. Si–O bonds are presumably formed across the interface between the glass and coupling agent. Coupling agents for more inert polymers like polyolefins are often acid-modified versions of the matrix polymer, with maleic acid–grafted polypropylene as a prime example.

More recently, an emerging technique for preparing polymer composites is by incorporating nano-sized inorganic fillers into polymeric materials. Several such

systems have recently been shown to be ideal candidates for various industrial applications because they have excellent stiffness and strength, high heat distortion temperature, and good scratch resistance [35–37]. Polymer nanocomposite thin films have also demonstrated improved adhesive properties. As a result, polymer nanocomposites have started to gain commercial acceptance in practical applications recently: for example, used in materials designing for microelectronics, optics, and coatings. In view of the strong industrial-application potential, considerable research and development interests have been generated, in both academic and industrial communities, to study polymer nanocomposites in relation to the selection and modification of nano-sized inorganic fillers for various polymer matrices of interest and to the determination of the optimum conditions for processing such materials [38–40]. The two classes of nano-sized inorganic fillers that have been extensively used and studied are clays and carbon nanotubes. Clays belong to the platelet type of fillers that have nanometer thickness and can be exfoliated, while carbon nanotubes have diameter in the nanometer range. Since such fillers possess high surface to volume ratios, they would greatly enhance the mechanical properties even though a low dosage of such fillers is used. This is because nano-sized fillers, either in the platelet or tube form, have a geometrical length scale comparable to the size of polymer molecules. As a result, this produces, for example, an excluded volume interaction with a flexible polymer that strongly reshapes the overall polymer conformation (Section 1.14). The entropy loss of the flexible chains in the vicinity of the nano-sized fillers is one of the physical reasons to drive the phase separation. The free volume available to nano-sized particles and the conformational change of the interacting polymer molecules, especially in the interfacial region, are the critical controlling factors for the surface modification, leading to enhanced mechanical properties [20,41,42].

---

## PROBLEMS

- 5-1** Toluene (molecular weight = 92, density =  $0.87 \text{ g/cm}^3$ ) boils at  $110.6^\circ\text{C}$  at 1 atm pressure. Calculate its solubility parameter at  $25^\circ\text{C}$ . [The enthalpy of vaporization can be approximated from the normal boiling point  $T_b$  (K) of a solvent from  $\Delta H_{(25^\circ\text{C})} = 23.7T_b + 0.020T_b^2 - 2950 \text{ cal/mol}$  (J. Hildebrand and R. Scott, *The Solubility of Nonelectrolytes*, 3rd ed, Van Nostrand Reinhold, New York, 1949).]
- 5-2** Calculate the solubility parameter for a methyl methacrylate–butadiene copolymer containing 25 mol% methyl methacrylate.
- 5-3** Calculate the solubility parameter for poly(vinyl butyl ether). Take the polymer density as  $1.0 \text{ g/cm}^3$ .
- 5-4** (a) A vinyl acetate/ethylene copolymer is reported to be soluble only in poorly hydrogen-bonded solvents with solubility parameters between 8.5

and  $9.5 \text{ (cal/cm}^3)^{1/2}$ . A manufacturer wishes to make solutions of this copolymer in Varsol No. 2 (a nonaromatic hydrocarbon distillate,  $\delta = 7.6$ , poorly hydrogen-bonded). Suggest another relatively low-cost solvent that could be added to the Varsol to increase its solvent power for the copolymer and calculate the composition of this mixed solvent.

(b) Would you expect this copolymer to form stable mixtures with polyethylene? Why or why not?

**5-5** Calculate the composition by volume of a blend of *n*-hexane, *t*-butanol, and dioctyl phthalate that would have the same solvent properties as tetrahydrofuran. (Use Table 5.4 and match  $\delta_P$  and  $\delta_H$  values.)

**5-6** The introduction of a minor proportion of an immiscible second polymer reduces the viscosity and elastic character of a polymer melt at the processing rates used in normal commercial fabrication operations [19]. It is necessary, also, that there be good adhesion between the dissimilar zones in the solid blend to obtain finished articles with good mechanical strength.

Suggest polymeric additives that could be used in this connection to modify the processing behavior of

(a) polyethylene melts.

(b) styrene–butadiene rubber (SBR).

**5-7** *Note:* (This problem is for **illustrative purposes only**. Methyl isobutyl ketone fumes have been reported to be **hazardous**.) A common solvent mixture for commercial nitrocellulose consists of the following:

Diluent (toluene) 50 parts by volume

“Latent” solvent (1-butanol) 13 parts by volume

“Active” solvent (mixture) 37 parts by volume

The “active” solvent mixture includes:

Methyl ethyl ketone (fast evaporation rate) 32%

Methyl isobutyl ketone (medium evaporation rate) 54%

Diethylene glycol monomethyl ether (slow evaporation rate) 14

From these data estimate whether tetrahydrofuran would be a solvent for this nitrocellulose polymer. Use Table 5.3.

**5-8** Consider a hypothetical binary blend composed of linear polymers A and B with  $DP_A = 1000$  and  $DP_B = 500$ . The Hildebrand solubility parameters of the polymers are  $\delta_A = -0.001 T + 10.0$  and  $\delta_B = -0.0008 T + 10.2$ , respectively, where  $\delta$  is in  $(\text{cal/cm}^3)^{1/2}$  and  $T$  is in K. The reference volume for the blend has a functional form of  $V_0 = 20 + 0.015 T$ . Here,  $V_0$  is in  $\text{cm}^3/\text{mol}$  while  $T$  is in K. Note that the universal gas constant  $R = 1.987 \text{ cal/mol K}$ .

(a) Determine  $\chi_{\text{critical}}$  for the blend;

- (b) Calculate  $\chi_{AB}$  at 200 K and 600 K based upon their Hildebrand solubility parameters;
- (c) Based upon the results obtained in part (b), what conclusion can you make on the phase behavior of the blend? Why?

- 5-9 Consider the following empirical expression for the Flory–Huggins interaction parameter  $\chi$

$$\chi = \frac{3.70 \times 10^{-2}}{T} + 7.64 \times 10^{-10} T^2$$

where  $T$  is the absolute temperature.

- (a) What are the units of the two constants in the above expression?
- (b) What type of phase behavior should one expect from the above expression? Why?
- (c) If a binary polymer blend containing polymers A ( $M_n = 275,000$  g/mol;  $\rho = 1.06$  g/cm<sup>3</sup>; molar volume of a repeating unit ( $v_A$ ) = 25 cm<sup>3</sup>/mol) and B ( $M_n = 650,000$  g/mol;  $\rho = 1.20$  g/cm<sup>3</sup>;  $v_B = 53$  cm<sup>3</sup>/mol), calculate  $\chi_{critical}$  based upon the geometric mean of the molar volumes of the repeating units of polymers A and B;
- (d) Plot  $\chi$  against  $T$  over the temperature range of 100 to 500 K and determine the UCST and LCST of the blend.
- 5-10 The weight fraction activity coefficient at infinite dilution (i.e., the concentration of the solvent in the polymer is very low),  $\Omega_1^\infty$ , can be measured by a technique so-called inverse gas chromatography. In a particular experiment,  $\Omega_1^\infty$  and the ratio of the specific volume of the solvent to that of the polymer,  $\nu_1/\nu_2$ , at 150 °C are measured to be 4.49 and 1.1, respectively. Also, the relationship between  $\Omega_1^\infty$  and the Flory–Huggins interaction parameter,  $\chi$ , is given by the following equation:

$$\ln \Omega_1^\infty = \ln \frac{\nu_1}{\nu_2} + 1 + \chi$$

Note that the activity of the solvent in the polymer,  $a_1$ , is given by the following equation:

$$a_1 = \Omega_1^\infty w_1 = \gamma_1 x_1$$

where  $w_1$  and  $x_1$  are the weight and mole fractions of the solvent and  $\gamma_1$  is the activity coefficient of the solvent in the polymer.

- (a) Are the solvent and polymer miscible under the above described conditions?
- (b) What is the volume fraction of the solvent in the polymer if  $w_1 = 0.002$ ?

- 5-11** It is generally observed that the Flory–Huggins interaction parameter depends not only on the temperature but also on the composition of a binary polymer solution. For solutions of polystyrene in cyclohexane, the Flory–Huggins interaction parameter is determined to have the following relation:

$$\chi = 0.2035 + \frac{90.65}{T} + 0.3092\phi + 0.1554\phi^2$$

where  $T$  is the temperature in the unit of K and  $\phi$  is the polymer volume fraction.

- (a) Assuming that volume change of mixing is negligible, what is the Gibb's free energy change of mixing 1 g of polystyrene with a number average molecular weight of  $10^5$  g/mol and 1 mol of cyclohexane (J/mol) at 400 K? The molar volumes of polystyrene and of cyclohexane are  $9.5 \times 10^4$  and  $108 \text{ cm}^3/\text{mol}$ , respectively. Note that  $R = 8.314 \text{ J/mol K}$ .
- (b) What is the critical Flory–Huggins interaction parameter of the polystyrene/cyclohexane system?
- (c) Does the polystyrene/cyclohexane system have a UCST or LCST?
- (d) Determine the theta temperature (K) at  $\phi = 0.1$ .
- 5-12** A composite consists of 45% by volume of continuous, aligned carbon fibers and an epoxy resin. The tensile strength and modulus of the fibers is 3000 Mpa and 200 GPa, respectively, while the corresponding parameters of the cured epoxy are 70 MPa and 2.5 GPa, respectively. Determine (a) which component of the composite will fail first when the material is deformed in the fiber direction, and (b) the failure stress of the composite.

---

## References

- [1] G. Scatchard, *Chem. Rev.* 8 (1931) 321.
- [2] J.H. Hildebrand, J.M. Prausnitz, R.L. Scott, *Regular and Related Solutions*, Van Nostrand Reinhold, New York, 1970.
- [3] P.A. Small, *J. Appl. Chem.* 3 (1953) 71.
- [4] K.L. Hoy, *J. Paint Technol.* 42 (541) (1970) 76.
- [5] S. Krause, *J. Macromol. Sci. Macromol. Rev.* C7 (1972) 251.
- [6] E.A. Grulke, in: J. Brandrup, E. Immergut (Eds.), *Polymer Handbook*, third ed., Wiley, New York, 1989, p. VII/519.
- [7] A. Beerbrower, L.A. Kaye, D.A. Pattison, *Chem. Eng.* (December 18, 1967) 118.
- [8] P.J. Flory, *J. Chem. Phys.* 9 (1941) 66010, 51 (1942)
- [9] M.L. Huggins, *J. Chem. Phys.* 9 (1941) 440; *Ann. N.Y. Acad. Sci.* 43, 1 (1942)
- [10] C.M. Hansen, *J. Paint Technol.* 39 (1967) 104511.
- [11] C.M. Hansen, *Ind. Eng. Chem. Prod. Res. Dev.* 8 (1969) 2.
- [12] P. Choi, T.A. Kavassalis, A. Rudin, *IEC Res.* 33 (1994) 3154.

- [13] P. Choi, T.A. Kavassalis, A. Rudin, *J. Coll. Interf. Sci.* 180 (1996) 1.
- [14] J.P. Teas, *J. Paint Technol.* 40 (1968) 519.
- [15] P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
- [16] L.H. Tung (Ed.), *Fractionation of Synthetic Polymers*, Dekker, New York, 1977.
- [17] E. Karbasheski, L. Kale, A. Rudin, H.P. Schreiber, W.J. Tchir, *Polym. Eng. Sci.* 31 (1991) 1581.
- [18] M.G. Pigeon, S. Rudin, *J. Appl. Polym. Sci.* 51 (1994) 303.
- [19] A. Rudin, *J. Macromol. Sci. Rev.* C19 (1980) 267.
- [20] D.R. Paul, C.B. Bucknall (Eds.), *Polymer Blends*, Wiley Interscience, New York, 2000.
- [21] J.T. Bergen, in: F.R. Eirich (Ed.), *Rheology*, vol. 4, Academic Press, New York, 1967.
- [22] W.D. Mohr, in: E.C. Bernhardt (Ed.), *Processing of Thermoplastic Materials*, Van Nostrand Reinhold, New York, 1959.
- [23] D.G. Baird, D.I. Collias, *Polymer Processing: Principles and Design*, Wiley (Interscience), New York, 1998.
- [24] P. Choi, H.P. Blom, T.A. Kavassalis, A. Rudin, *Macromolecules* 28 (1995) 8247.
- [25] P. Choi, *Polymer* 41 (2000) 8741.
- [26] J.Z. Fan, M.C. Williams, P. Choi, *Polymer* 43 (2002) 1497.
- [27] G.H. Fredrickson, A.J. Liu, F.S. Bates, *Macromolecules* 27 (1994) 2503.
- [28] H.W. Starkweather Jr., *J. Appl. Polym. Sci.* 20 (1980) 364.
- [29] E. Nolley, J.W. Barlow, D.R. Paul, *Polym. Eng. Sci.* 25 (1980) 139.
- [30] A. Rudin, D.A. Loucks, J.M. Goldwasser, *Polym. Eng. Sci.* 74 (1980) 741.
- [31] C.M. Robeson, J.E. McGrath, *Polym. Eng. Sci.* 17 (1977) 300.
- [32] M. Morton, *Am. Chem. Soc. Polym. Div. Preprints* 10 (2) (1969) 512.
- [33] A.R. Shultz, B.M. Beach, *J. Appl. Polym. Sci.* 21 (1977) 2305.
- [34] G. Kraus, K.W. Rollman, *J. Polym. Sci. Phys. Ed.* 14 (1976) 1133.
- [35] A. Usuki, M. Kawasumi, Y. Kojima, A. Okada, T. Kurauchi, O. Kamigaito, *J. Mater. Res.* 8 (1993) 1174.
- [36] A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, et al., *J. Mater. Res.* 8 (1993) 1179.
- [37] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, et al., *J. Mater. Res.* 8 (1993) 1185.
- [38] C.M. Chan, J. Wu, J.X. Li, Y.K. Cheung, *Polymer* 43 (2002) 2981.
- [39] O. Becker, R. Varley, G. Simon, *Polymer* 43 (2002) 4365.
- [40] J.H. Park, S.C. Jana, *Polymer* 44 (2003) 2091.
- [41] D. Qian, E.C. Dickey, R. Andrews, T. Rantell, *Appl. Phys. Letters* 76 (2000) 2868.
- [42] M. Cadek, J.N. Coleman, V. Barron, K. Hedicke, W.J. Blau, *Appl. Phys. Letters* 81 (2002) 5123.