

Polymer Compatibility

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Synopsis

Bohn¹ has compiled a list of polymer pairs on which compatibility studies have been reported. The list contains 13 polymer pairs for which, according to Bohn, compatibility as solids may be considered to be definitely established, at least within some regions of proportions. The approach used here is based on calculations which provide a value whose magnitude apparently differentiates between mixtures in Bohn's list which are either compatible as solids or incompatible. Data calculated on mixtures of styrene-acrylonitrile copolymers not included in Bohn's list systematize according to the same classification.

INTRODUCTION

Bohn¹ has compiled a list of polymer pairs on which compatibility studies have been reported. The list, which has been referred to by others²⁻⁴ when discussing polymer compatibility, contains 13 pairs for which, according to Bohn, compatibility as solids may be considered to be definitely established in at least some regions of proportions. Brodsky² has suggested a "degree of compatibility" concept using as a basis the magnitude as well as the sign of the free energy of mixing. He suggests that the degree of compatibility would decrease with increasing free energy of mixing. It can be noted that, if the system consists of two dissimilar polymers in the absence of a solvent, an approximation of the free energy of mixing may be obtained from calculation of the heat of mixing.^{4,5} The approach used here is based on calculations which provide a value whose magnitude apparently differentiates between polymer mixtures in Bohn's list which are either compatible as solids or incompatible.

The literature provides examples of others^{4,6} who have used the approach of providing a value whose magnitude is taken as a guide in a search for compatible polymer pairs. For instance, in a recent review article, Krause⁴ presents a method of calculation for predicting compatibility of polymers in bulk. It consists of a comparison of the calculated values of χ_{AB} , the interaction parameter between two polymers, and of $(\chi_{AB})_{cr}$, the critical point on a phase diagram for a binary system, which indicates the limits of compatibility. If χ_{AB} is greater than $(\chi_{AB})_{cr}$, the two polymers should be incompatible at some percentage composition. The greater the difference between the two values of χ_{AB} , the smaller the range of composition in which the polymers will be compatible. Pazonyi and Dimitrov⁶

calculated a value for which the heat of mixing, ΔH , is less than the entropy term, $T\Delta S$. They conclude that, if the difference between the cohesive energy densities of the two components is smaller than 0.016 cal/cm^3 , there exists the possibility of mutual solution, whatever the sign of the heat of mixing turns out to be.

The approach used here in providing a value is based on the use of a relationship suggested by Gee.⁷ A modification of this relationship has been employed⁸ as a means for providing values of the energy expended in the various steps in a diffusion study. The approach is considered helpful since it permits calculations based on polymer concentration in the system, solubility parameter, and density; the weight of an average repeating unit is used here, in place of information about the molecular weight of the polymer of interest.⁴

THEORY

Common underlying principles and mechanisms are considered in discussions of polymer compatibility,⁵ the permeation process,⁹⁻¹⁴ adhesion,¹⁵ and adsorption of polymers at an interface.¹⁶⁻¹⁸ The analogous mechanisms involve an interaction between segments of a polymer with a substrate which can be the polymer itself, a diluent, or another polymer, organic or inorganic. Interactions may occur between segments of two dissimilar polymers of equal size and shape leading to mutual diffusion of the polymers or, what is considered more likely, intermingling at the boundaries of the segments leading to adhesion.

Equation (1) has been used⁸ as a means for providing values of the energy for the absorption, diffusion, and desorption steps in the pressure-induced diffusion of 12 organic liquids through a highly swollen rubber membrane.¹⁴ The equation is a modification of a relationship suggested by Gee⁷ who has shown that the degree of swelling of vulcanized rubber by various liquids is related to the heats of mixing which, in turn, are related to the difference between the cohesive energy densities of the liquid and rubber:

$$\Delta H_M = (V_o(\delta_o - \delta_r)^2(1 - v_o)^2)^{1/2} \quad (1)$$

where V and δ are the molar volume and solubility parameter of the liquid O and the rubber r and the term $(1 - v_o)$ represents the volume fraction of rubber present when the rubber is fully swollen by that liquid. Equation (1) consists of three parts: (1) the molar volume of the liquid which is related to the molecular dimensions of the penetrant; (2) the difference in the solubility parameters between the penetrant and the rubber which is a measure of the interaction between them, and (3) the term $(1 - v_o)$ which provides a measure of the concentration of the penetrant available for absorption, diffusion, and desorption. Based on the limited data available, the use of this equation in the diffusion study afforded consistent results which appear to differentiate among different types of penetrant liquids.

The similarity of the underlying principles and mechanisms considered in the permeation and absorption processes and the use of analagous criteria for polymer compatibility with these principles suggested that the Gee relationship might also be useful in differentiating between polymer systems that are compatible as solids from those that are not. In Bohn's list, in most instances, compatible polymer pairs were prepared by mixing the polymers in the melt. Mixing in the melt is not a necessary condition nor does it assure obtaining polymer pairs compatible as solids. Nevertheless, in the molten state, the polymers exhibit reduced viscosity affording the possibility of adsorption at the surfaces and mutual diffusion. It is realized that thermodynamic equilibrium may not be reached during mixing because of a slow rate of diffusion and limits of time and shear inherent in any mixing operation. The primary assumption, then, is that mixing in the melt provides an opportunity for interactions between polymers and that eq. (1), then, can be taken to represent the potential energy available to the system for interactions leading to adsorption and diffusion. Since our interest lies in those systems that would be expected to be compatible as solids at room temperature, values at 25°C were used for the density and solubility parameter of the polymer. This approach simplified the calculations since the variation in molar volume and solubility parameter with temperature could be neglected.

Equation (1) was rewritten as

$$\Delta H_M = (V_1(\delta_1 - \delta_2)^2(1 - v_1)^2)^{1/2} \quad (2)$$

where V_1 and v_1 are the molar volume and volume fraction of polymer 1, respectively, and the term $(1 - v_1)$ represents the volume fraction of polymer 2 present in the mixture. Since in every mixture there is a given weight, x , of polymer, $(x_1/M_1)/\rho_1 = V_1$ represents the molar volume fraction of polymer 1, where M and ρ are the molecular weight of an average monomer unit and polymer density, respectively. Generally, V_1 is taken as the molar volume of the entire system. The use here of V_1 as the molar volume fraction of polymer 1 present in the system is considered valid since we wish to study the effect of changes in the concentration of volume segments of polymers in a system on the energies of interaction between them. The volume fraction v_1 of polymer 1 present in the system is given by

$$v_1 = \frac{(x_1/M_1)/\rho_1}{(x_1/M_1)/\rho_1 + (x_2/M_2)/\rho_2} \quad (3)$$

and

$$1 - v_1 = \frac{x_2 M_1 \rho_1}{x_1 M_2 \rho_2 + x_2 M_1 \rho_1} \quad (4)$$

Bearing in mind that $x_1 + x_2 = 1$, and substituting this value into (4) and (2), eq. (5) is obtained after usual algebraic operations:

$$H_M = \{x_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 [(x_2/(1 - x_2) M_2 \rho_2 + (1 - x_1) M_1 \rho_1)^2]^{1/2}\}^{1/2}. \quad (5)$$

The usefulness of eq. (5) in pointing up polymer pairs compatible as solids was tested initially using the data of Bohn¹ who listed the polymer pairs under the headings of first and second components. In the use of eq. (5), polymer 1 was taken as the one listed as the first component. Although slight differences were observed depending on which component was selected as component 1, values between approximately 1×10^{-3} and 10×10^{-3} cal were found to be limiting between polymer systems compatible as solids from those that are not. Values for x_1 , the weight fraction of component 1, was varied between the limits set forth in Bohn's tables except that, here, values for $x_1 = 0$ or 1.0 ($x_2 = 0$) are not defined.

In order to use eq. (5), values are needed for the solubility parameter, density, and molecular weight of an average unit of the polymer. For the homopolymers, literature values for δ and ρ were used as given, for example, in references 19–21; M was taken as the molecular weight of a repeat unit. For the copolymer, use was made of eq. (6)²² to calculate the necessary values:

$$\delta_x = \frac{(n_1 M_1^2 / \rho_1) \delta_1 + (n_2 M_2^2 / \rho_2) \delta_2}{\{n_1 M_1 + n_2 M_2\} \{ (n_1 M_1^2 / \rho_1) + (n_2 M_2^2 / \rho_2) \} [1 / \rho_x]}^{1/2} \quad (6)$$

where n refers to the number of moles, and the subscripts 1, 2, and x refer, in turn, to components 1, 2, and mixture. The molecular weight of an average monomer unit was taken as $n_1 M_1 + n_2 M_2 = M_x$.²³ If literature data were unavailable, the density of the copolymer was taken as $n_1 M_1 / \rho_1 + n_2 M_2 / \rho_2 = 1 / \rho_x$. In addition, for the acrylonitrile segments in its styrene and butadiene copolymers, a value of $\delta = 13.26$ was used.²² Finally, for butadiene, $\delta = 8.36$ was used when it was present as a copolymer with either styrene or acrylonitrile, and $\delta = 7.73$ as a homopolymer.²²

RESULTS AND DISCUSSION

Table I shows the 13 polymer pairs for which, according to Bohn,¹ compatibility as solids may be considered to be definitely established in at least some regions of proportions. The first ten polymer pairs were tested. Two of the remaining mixtures were not tested because one of the components was ill-defined, ebonite, polybutadiene (Russian). The remaining system, polystyrene–poly(α -methylstyrene) is also listed under polymeric systems incompatible as solids. The table lists, in addition, the weight fraction of the first component and method of preparation of the polymer pair. For convenience, values for M , ρ , and δ used here are given. The table shows that, in most cases, compatible polymer pairs were prepared by mixing in the melt. There are two examples of polymers prepared by casting from solution and one example of a polymer prepared by grafting. The one example of a block copolymer is questionable.

Figure 1 shows the effect of change in weight fraction of component 1 (Table I) on the value calculated employing eq. (5). The weight fraction of the components of the polymer mixture was varied within the range

TABLE I
 Polymer Mixtures Compatible as Solids^a

Polymer	First component			Polymer	Second component			Nature of mixture ^b	
	M	ρ , g/cm ³	δ , (cal/cm ³) ^{1/2}		M	ρ , g/cm ³	δ , (cal/cm ³) ^{1/2}		Wt-% of component 1
1. PVC	62.50	1.40	9.52	Bu/AN 66.7/33.3	53.75	0.976	9.68	90-20	L ₁ M
2. PVAc	86.09	1.19	9.56	PMA	87.10	1.22	10.0	50	L ₁ M
3. Bu/AN 82/18	53.00	1.07	9.09	same 60/40	53.68	1.10	10.18	0-100	M
4. CPE 62% Cl	98.83	1.42	9.90	same 66% Cl	152.28	1.50	9.80	0-100	L ₁ M
5. St/AN 80/20	93.91	1.07	9.50	Bu/AN 65/35	53.76	0.981	9.78	70-100	M
6. PMMA	100.23	1.17	9.71	PEA	101.15	1.12	9.42	21	P
7. PVAc	86.09	1.19	9.56	VC/VAc 90/10	64.86	1.38	9.53	<40-50<	M
8. PSt	104.12	1.05	9.1	Bu/St 75/25	66.01	0.92	8.48	\leq 40	M
9. St/AN 79.5/20.6	91.90	1.07	9.64	same 76/24	93.70	1.07	9.55	50	M
10. Bu/AN 60/40	53.68	1.10	10.0	cellulose acetobutyrate	598	1.25	10.6	<20-90<	M
11. Natural rubber				PBu (Russian)				0-100	M
12. Ebonite				polysulfide				95-80	M
13. PSt ^c				poly(α -methylstyrene)				44-50	B

^a Taken from Bohn.¹^b Taken from Bohn¹; L = mixtures from solution; M = mixture from melt; P = graft copolymer; B = block copolymer.^c At 50% polystyrene, this mixture is listed under polymeric systems incompatible as solids.¹

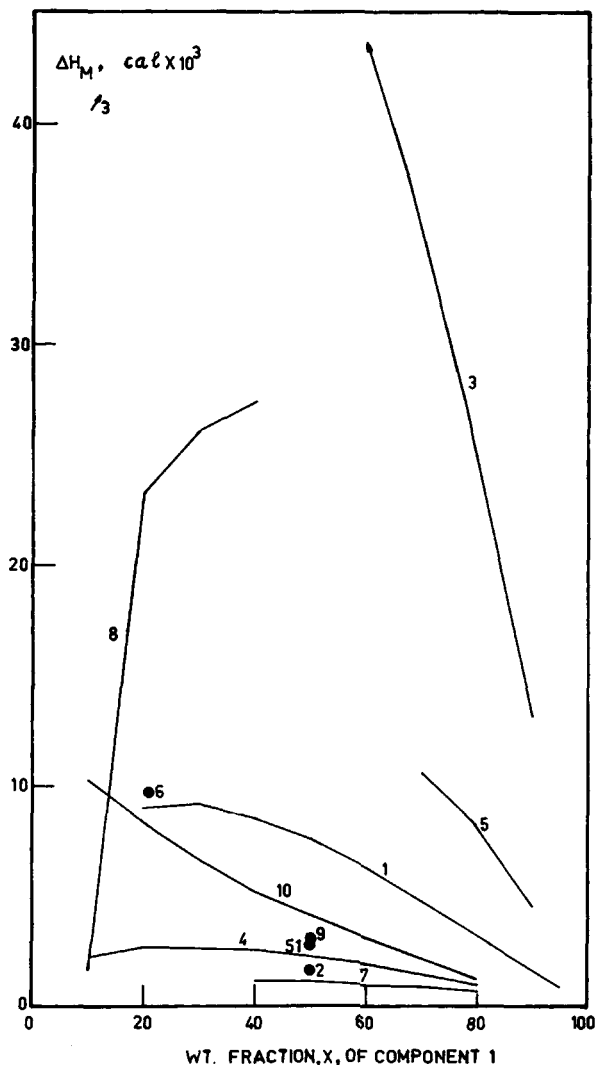


Fig. 1. Change in calculated value, eq. (5), with weight fraction of component 1. For mixtures compatible as solids numbers 1-10 refer to polymer pairs listed in Table I (Bohn's list¹) and number 51, to a combination of styrene-acrylonitrile copolymers given in Table III (Molau's list²⁴). Polymer pair shown as no. 9 (Table I) is the same as no. 52 (Table III).

shown in the table except for values of $x_1 = 0$ or $= 1.0$. The results show that, for the compatible polymer pairs, in 8 out of 10 instances, the values (eq. 5) vary from about 1×10^{-3} to 10×10^{-3} cal. System 3, consisting of two butadiene-acrylonitrile copolymers but with different acrylonitrile contents is classified as compatible by Bohn¹ but ambiguous by Krause.⁴ The results obtained here indicate that this system does not fall in with the general class of compatible pairs. As shown previously,²² difficulties are

TABLE II
Polymeric Systems Incompatible as Solids^a

Polymer	First component			Second component			Nature of mixture ^b	
	M	ρ , g/cm ³	δ , (cal/cm ³) ^{1/2}	Polymer	M	ρ , g/cm ³		δ , (cal/cm ³) ^{1/2}
21. PE	28.02	0.90	7.9	PIB	56.10	0.84	7.5	20-80 M
22. PMMA				PVAc				70, 50 L
23. Natural rubber	68.11	0.80	8.0	Bu/St 75/25	66.01	0.92	8.48	
24. PSSt				PBu	54.09	0.90	7.73	>75
25. PMMA				PMA				25-50 M, P, L
26. PSSt				Bu/AN 75/25	53.83	0.96	9.48	20-30 M
27. PSSt				PVC				50 M
28. PSSt				PE				0-30 M, P
29. PE				PP	42.04	0.905	8.2	5-95 B, L
30. PSSt				PMA				50, 80 M, L, P
31. PVC				Bu/St 75/25				40-80 M
32. Nylon 6	113.13	1.15	11.18	PMMA				77, 65 P
33. Nylon 6				PVAc				87 P
34. Nylon 6				PMA				85-76 P
35. Nylon 6				PEA	101.15	1.12	9.42	91, 80 P

^a Taken from Bohn.¹

^b Taken from Bohn¹; L = mixtures from solution; M = mixture from melt; P = graft copolymer; B = block copolymer.

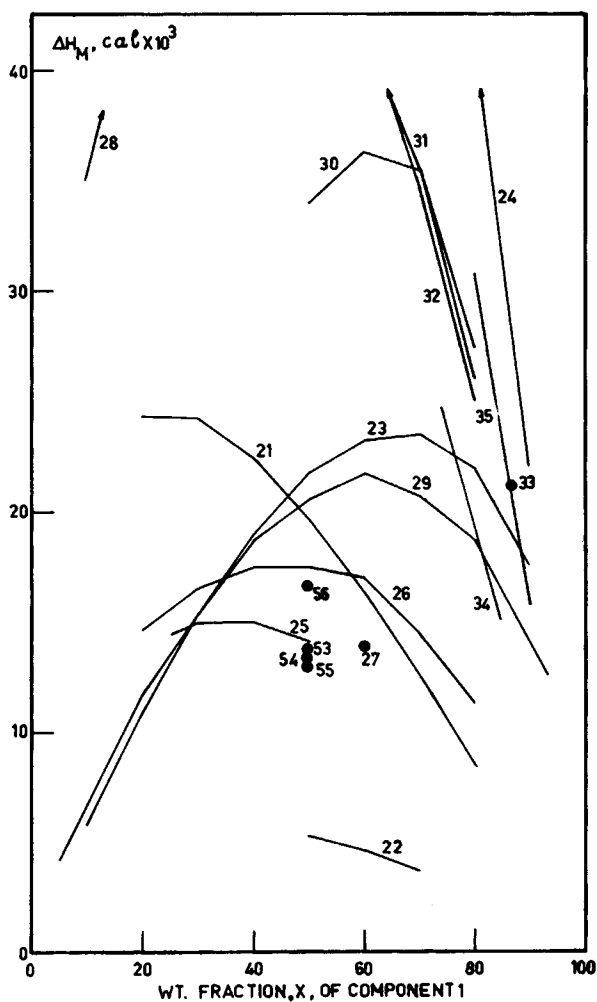


Fig. 2. Change in calculated value, eq. (5), with weight fraction of component 1. For mixtures incompatible as solids, numbers 21–35 refer to polymer pairs given in Table II (Bohn's list¹), and numbers 53–56, to those listed in Table III (Molau's list²⁴).

encountered when trying to calculate values of δ for various butadiene copolymers. It may be that the difference between the solubility parameter of the two copolymers is smaller than calculated. Similarly, system 8, consisting of polystyrene and butadiene–styrene copolymer (75/25), does not appear to fall into this general class. Finally, system 7 presents an anomaly in that mixtures of poly(vinyl acetate) with a copolymer of vinyl chloride and 5–10% vinyl acetate are compatible at some ratios and incompatible at some intermediate ones. The presence of a homogeneity gap is not indicated here.

TABLE III
Styrene-Acrylonitrile Polymer Pairs^a

First St/AN component				Second St/AN component				Compatibility	
AN, %	<i>M</i>	ρ , g/cm ³	δ , (cal/cm ³) ^{1/2}	AN, %	<i>M</i>	ρ , g/cm ³	δ , (cal/cm ³) ^{1/2}	yes	no
51. 24.0	91.90	1.07	9.64	25.5	91.10	1.07	9.66	+	
52. 20.6	93.70	1.07	9.55	24.0				+	
53. 25.5				38.9	90.80	1.08	10.03		+
54. 14.2	96.87	1.06	9.39	29.1	89.26	1.07	9.75		+
55. 4.6	101.77	1.05	9.19	20.6					+
56. 4.6				24.0					+

^a Data from Molau.²⁴

Table II shows 15 of the 46 polymer systems listed by Bohn¹ as incompatible as solids. Given also is the supplementary information provided in Table I. As indicated, despite the fact that in approximately half the cases the polymer pairs were prepared by mixing in the melt, the mixtures were incompatible as solids. Figure 2 shows that for these mixtures, in 14 out of 15 instances the results (eq. 5) are smaller than 10×10^{-3} cal. The polymer pair consisting of poly(methyl methacrylate) and poly(vinyl acetate) (no. 22) is considered incompatible by Bohn¹ and incompatible or ambiguous by Krause.⁴ According to the calculations carried out here, the system would be expected to be compatible.

Molau²⁴ studied the compatibility of mixtures of styrene-acrylonitrile copolymers. The polymer pairs are shown in Table III. The one listed as no. 52 was included in Bohn's table (item 9). The polymer pair consisting of styrene copolymers containing 24% and 25.5% acrylonitrile, respectively (no. 51), is classified as compatible by Molau. The value calculated using eq. (5) falls in with the those calculated for the other polymer mixtures compatible as solids (Fig. 1). The remaining four polymer mixtures were incompatible, according to Molau. These pairs fall in with the mixtures incompatible as solids (Fig. 2).

The subject of polymer compatibility is of theoretical interest and of importance technologically. Establishing the existence of compatible polymer pairs is one problem. An additional task for the investigator is the selection of polymer pairs. Based on a criterion of the lists used here, eq. (5) apparently provides a basis for selecting polymer pairs that may be compatible as solids.

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