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Miscibility of Poly(acrylonitrile-*co*-styrene) with Poly[styrene-*co*-(maleic anhydride)] and Poly[styrene-*co*-(*N*-phenylmaleimide)]

Yuji Aoki

Yokkaichi Research and Development Department, Mitsubishi Monsanto Chemical Co. Ltd., Toho-cho, Yokkaichi, Mie 510, Japan. *Received June 12, 1987*

ABSTRACT: Miscibility of blends of poly(acrylonitrile-*co*-styrene) with poly[styrene-*co*-(maleic anhydride)] and poly[styrene-*co*-(*N*-phenylmaleimide)] was determined by measurement of their glass transition temperatures by dynamic mechanical testing. It was found that poly(acrylonitrile-*co*-styrenes) are miscible with poly[styrene-*co*-(maleic anhydride)s] and poly[styrene-*co*-(*N*-phenylmaleimide)s] within specific ranges of copolymer composition for each blend. The boundaries between domains of miscibility and immiscibility were expressed by two straight lines intersecting at the origin, where the abscissa and ordinate represent the compositions of the respective copolymers in volume fraction. From the binary interaction model for copolymer mixtures, segmental interaction parameters between the different monomer units were estimated from these data and were found to be positive for all pairs. No attractive interactions were found between the acrylonitrile and maleic anhydride or *N*-phenylmaleimide. Miscibility of these blends is due to a repulsion between the two different monomer units comprising the copolymer.

Introduction

Studies of miscibility in polymer blends have been reported in recent years. It is generally agreed that the thermodynamic basis is an exothermic heat of mixing, since entropic contributions are so small in high molecular weight polymer blend systems. It is suggested that specific intermolecular interactions, that is, hydrogen bonding and n–π complex formation, are responsible for the exothermic heat of mixing.[1,2]

Recently, it has been demonstrated that systems consisting of a homopolymer and a copolymer or two different copolymers are miscible for a certain range of copolymer composition even though the combinations of their corresponding homopolymers are immiscible. It has been proposed that miscibility of copolymers is due to a repulsion between the two different monomer units comprising the copolymer,[3-5] and in a meanfield approach the overall Flory–Huggins interaction parameter between the two polymers can be simply expressed in terms of the respective segmental interaction parameters. ten Brinke et al.[4] extended this formulation to mixtures of two different copolymers. Paul and Barlow[5] and Shiomi et al.[6] applied it to blends of two random copolymers having a common monomer.

There have been many studies of miscibility of poly(acrylonitrile-*co*-styrene) (AS) with a homopolymer and

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Table I
Styrene Contents, Molecular Weights, and Densities of Copolymers Used

sample	St content wt %	St content mol %	$M_w/10^4$	M_w/M_n	density, g/cm³
PS	100	100	26.0	2.0	1.052
AS-15	85.1	74.4	12.8	2.2	1.070
AS-20	80.5	67.8	8.9	1.7	1.073
AS-27	73.5	58.5	8.7	2.2	1.077
AS-30	71.3	55.9	8.0	2.2	1.079
AS-33	67.7	51.7	6.3	2.1	1.081
AS-40	61.3	44.7	5.8	1.9	1.084
AS-55	45.0	29.4			
M-3(SMA)	84.7	83.9	18.5	2.0	1.098
M-9(SMA)	69.8	68.5	17.1	2.1	1.174
P-90(SPMI)	65.3	75.8			1.125
P-91(SPMI)	58.1	69.8			1.150
P-93(SPMI)	44.0	56.6	27.0[a]	2.0	1.196

[a] The value is not corrected by the method by Schultz and Beach.

a copolymer. It has been reported that AS is miscible with poly(methyl methacrylate) (PMMA),[7-9] poly(ε-caprolactone) (PCL),[10,11] poly[styrene-*co*-(maleic anhydride)] (SMA),[12-15] and poly[(methyl methacrylate)-*co*-(*N*-phenylmaleimide)],[16] when the acrylonitrile (AN) content of AS is within a specific range. For example, AS containing 8–28 wt % AN is miscible with PCL.[11] Another example is AS/SMA blends. Paul and Barlow[5] and Shiomi et al.[6] analyzed the miscibility of AS/SMA blends using the data by Hall et al.[12] and estimated segmental interaction parameters. They concluded that the segmental interaction parameter between the acrylonitrile and maleic anhydride monomer units is negative, in other words, the two monomer units have an attractive interaction. However, they used the copolymer composition in weight fraction instead of volume fraction. The copolymer composition should be used in the volume fraction to estimate segmental interaction parameters.

Miscibility of AS with other (co)polymers seems to be due to a strong repulsion between acrylonitrile and styrene monomer units. If this is true, there should be found other miscible AS blend systems. To find the new miscible blends, it is necessary to obtain segmental interaction parameters of comonomer unit pairs.

In this paper, miscibility of AS/SMA blends and AS/poly[styrene-*co*-(*N*-phenylmaleimide)] (SPMI) blends having various copolymer compositions was measured by dynamic mechanical testing. The densities of these copolymers and their blends were also measured. The isothermal boundaries of AS/SMA and AS/SPMI blends were obtained. Segmental interaction parameters between the different monomer units were estimated by using binary interaction models and the solubility parameter theory for the copolymer mixtures.

Experimental Section

1. Materials. The ASs with various AN contents were prepared by radical polymerization of styrene monomer with a particular composition of AN monomer. The SMAs and SPMIs were also prepared by radical polymerization. Table I summarizes the composition, molecular weight, and density for these copolymers used in this work. AN content (AN%) of AS and *N*-phenylmaleimide content (PMI%) of SPMI were measured by elementary analysis (Yanako, CHN Coder). The maleic anhydride content (MA%) was measured on a coulometric titrator (Mitsubishi Chemical Industry Co. Ltd., Model CT-01). The molecular weights and molecular weight distribution were determined by using GPC (Waters Associates, ALC/GPC Model 150C). The GPC system was calibrated by using standard polystyrene samples. Measured molecular weights of the AS and SMA samples were corrected to account for the composition in the copolymers by the method used by Schultz and Beach[17] with the assumption that molecules having equal contour lengths elute at equal volume. The weight-average molecular weight (M_w) of several samples was determined by low-angle laser light scattering (Chromatix, KMX-6). The M_ws by low-angle laser light scattering were almost equal to those by GPC.

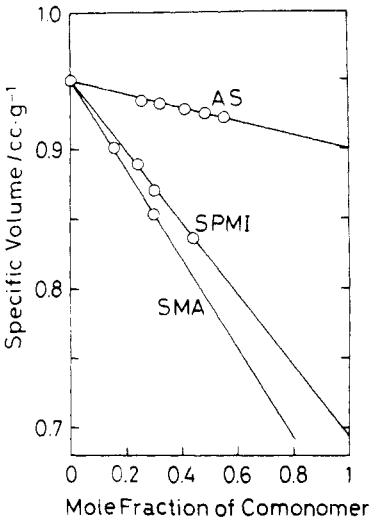

Figure 1. Specific volumes of AS, SMA, and SPMI plotted against mole fraction of AN, MA, and PMI.

2. Film Preparation. Blends were prepared by a melt blending method using a Brabender Plastograph at 200–240 °C for about 5 min. Films were pressed between steel sheets in the range 190–240 °C for 5 min and then quenched to room temperature. All the AS/SMA blends were pressed at 190 °C. AS/SPMI blends were pressed at 190–240 °C according to their composition. Film thickness of about 0.1 cm was used for density and dynamic mechanical measurements.

3. Measurements. The densities of polymer films were measured by the use of a gradient column composed of water and sodium chloride. All measurements were made at 23 °C. The resolution of the gradient column was 5×10^{-4} g/cm³ and the reproducibility of density measurements was within 1×10^{-3} g/cm³ for samples prepared at different times. The average of three measurements for each sample was taken as the experimental value.

Dynamic mechanical measurements were made to test sample miscibility by using a viscoelastic spectrometer (Iwamoto Seisakusho Co.) at a heating rate of about 1 °C/min and frequency of 20 Hz. Measurements were begun at 23 °C and continued until the sample became too soft to be tested. The glass transition temperature (T_g) is specified in this study as the temperature at which the loss modulus E'' is a maximum.

Results and Discussion

1. Density. The densities of the component copolymers and their blends were measured to calculate the copolymer composition in volume fraction. The densities of the component copolymers used in this work are tabulated in Table I. Figure 1 shows the specific volumes of AS, SMA, and SPMI plotted against mole fraction of AN, MA, and PMI. It is clear that the specific volumes of these copolymers are linear functions of mole fraction of the comonomers.[18] By extrapolation of the straight lines to mole fraction of unity, each specific volume of comonomer can be estimated to be 0.900, 0.630, and 0.694 cm³/g for AN, MA, and PMI, respectively. It was reported that the specific volume of polyacrylonitrile is 0.847 cm³/g at 25 °C.[19] The specific volume of the AN unit in AS is larger than that of polyacrylonitrile. We suppose that this discrepancy is due to semicrystallinity of polyacrylonitrile.

Figure 2 shows the densities and specific volumes of the M-9/AS-30 blends plotted against weight fraction of M-9.

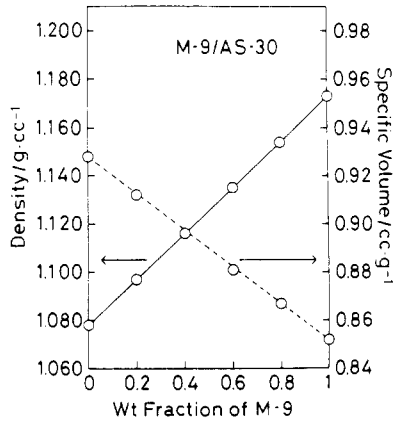

Figure 2. Densities and specific volumes of the M-9/AS-30 blends plotted against weight fraction of M-9.

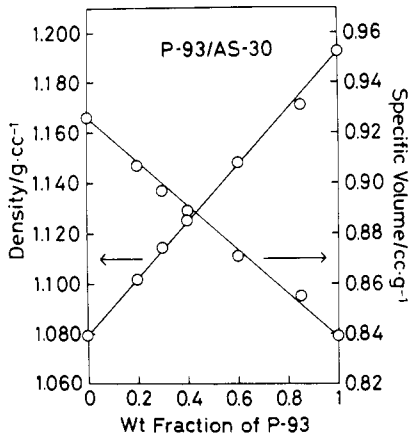

Figure 3. Densities and specific volumes of the P-93/AS-30 blends plotted against weight fraction of P-93.

The observed values (open circles) are in excellent agreement with calculated ones based on the rule of volume additivity (solid line). Almost identical results are obtained for the P-93/AS-30 blends (Figure 3). It can be concluded from the density measurements that the excess volume of mixing is very small and does not exceed the magnitude of experimental uncertainty, namely, $\pm 5 \times 10^{-4}$ g/cm^3, and the density of each comonomer in blends is identical with that in the copolymer.

2. Dynamic Mechanical Properties. Figure 4a shows the temperature dispersions of the dynamic storage modulus E' and loss modulus E'' for pure AS-15, P-93, and their blend. For pure AS-15 the maximum at about 120 °C on the E'' curve arises from the glass transition of AS-15. In the temperature range of this transition, the E' decreases markedly. For pure P-93 the transition occurring above 200 °C is the glass transition. The T_g occurs at 220 °C on the E'' curve. For the P-93/AS-15 blend (closed circles) the E'' curve has two maxima and the E' curve decreases in the range of corresponding temperatures. The maximum temperature of the E'' curve at low temperature coincides with the glass transition temperature on the E'' curve of pure AS-15. The existence of two glass transitions is considered to be confirmation of the immiscibility of the P-93/AS-15 blend.

Figure 4b–e shows the temperature dispersions of E' and E'' for P-93 blends with AS-20, AS-27, AS-33, and AS-40. Each blend exhibits a single glass transition at almost the same temperatures. These maxima corresponding to the glass transition on the E'' curves exist at a temperature intermediate between those of the respective pure components, although they are somewhat broadened. These facts are evidence of miscibility of these P-93/AS blends.

Figure 4f shows the temperature dispersions of E' and E'' for the P-93/AS-55 blend. The dynamic mechanical properties of the P-93/AS-55 blend are similar to those of the P-93/AS-15 blend. The E'' curve of the P-93/AS-55 blend has two maxima due to the glass transitions of each component copolymer. This is evidence of the immiscibility of the P-93/AS-55 blend.

Based on glass transition measurements, P-93 was found to be miscible with AS containing AN contents ranging from 20 to 40 wt %. The reason why the AN content in AS influences blend miscibility will be discussed in a later section.

Figure 5a shows the temperature dispersions of E' and E'' for the M-9/AS-20 blends. The blend containing 80 wt % M-9 displays two maxima on the E'' curve. For blends containing 60 wt % or less M-9, two maxima on the E'' curves cannot be observed clearly, but E'' curve maxima are very broad. The glass transition temperatures of these blends are somewhat higher than that of pure AS-20, indicating the incorporation of some M-9 in the AS. The partial mixing of a small quantity of M-9 in the AS phase may be possible, as evidenced from the broadness of the E'' curves. The blends are only partially miscible and may be the boundaries between domains of miscibility and immiscibility.

Figure 5b shows the temperature dispersions of E' and E'' for the M-9/AS-30 blends. The E'' curve of each blend has only a single maximum corresponding to the T_g. The E'' curve maxima are as high and sharp as those of the component copolymers. The T_g shifts to a higher temperature with increasing M-9 content. These simple compositionally dependent glass transitions are evidence of miscibility. The dynamic mechanical properties of the M-9/AS-27 and M-9/AS-33 blends were similar to those of the M-9/AS-30 blends. Each blend displays a single glass transition, which is evidence of miscibility.

Figure 5c shows the temperature dispersions of E' and E'' for the M-9/AS-40 blends. The E'' curve of the M-9/AS-40 blends has two maxima due to the glass transitions of each component copolymer. This is evidence of the immiscibility of the M-9/AS-40 blends. M-9 has found to be miscible with AS containing AN contents ranging from about 20 to 35 wt %.

3. Miscibility Maps of AS/SPMI and AS/SMA. The miscibility of AS with SMA and SPMI containing various styrene content was determined by the glass transition temperature behavior. Figures 6 and 7 show the miscibility maps of AS/SMA and AS/SPMI blends. Here, the abscissa and ordinate represent the compositions of the respective copolymers in volume fraction. The volume fraction was obtained from the specific volumes of each comonomer by density measurements. Open circles denote miscible, half-closed circles partially miscible, and closed circles immiscible blends. The boundaries between domains of miscibility and immiscibility are expressed by straight lines for both blend systems.

Here we will describe a thermodynamic interpretation of the miscibility maps. In the first-order Flory–Huggins formulation for polymer mixtures,[20] the free energy of mixing ΔG at a temperature T for a blend of r_1-mers and r_2-mers can be written

$$\Delta G/RT = (\phi_1/r_1) \ln \phi_1 + (\phi_2/r_2) \ln \phi_2 + \chi_{blend}\phi_1\phi_2 \quad (1)$$

where R is the gas constant, ϕ_1 and ϕ_2 are the volume fractions of r_1-mer and r_2-mer in the blend, and χ_{blend} is the net segmental interaction parameter between the two polymers. Neglecting the combinatorial entropy term for the blend with high molecular weights, the miscibility depends simply on the sign of χ_{blend}; if χ_{blend} is negative,

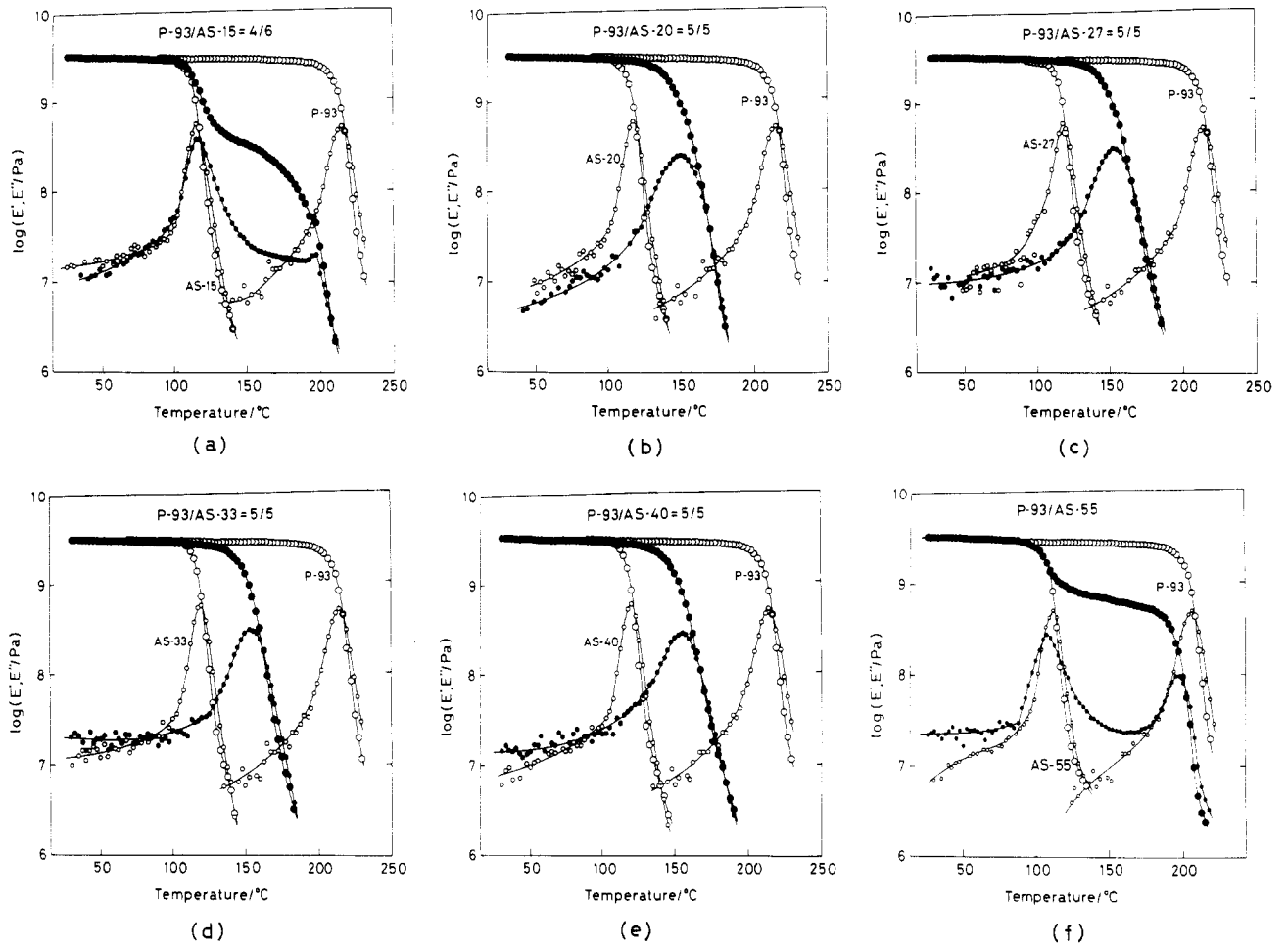

Figure 4. Temperature dispersions of the dynamic storage (E') and loss (E'') moduli at 20 Hz for P-93 blends with AS-15 (a), AS-20 (b), AS-27 (c), AS-33 (d), AS-40 (e), and AS-55 (f). Open circles denote pure copolymers, and closed circles their blends.

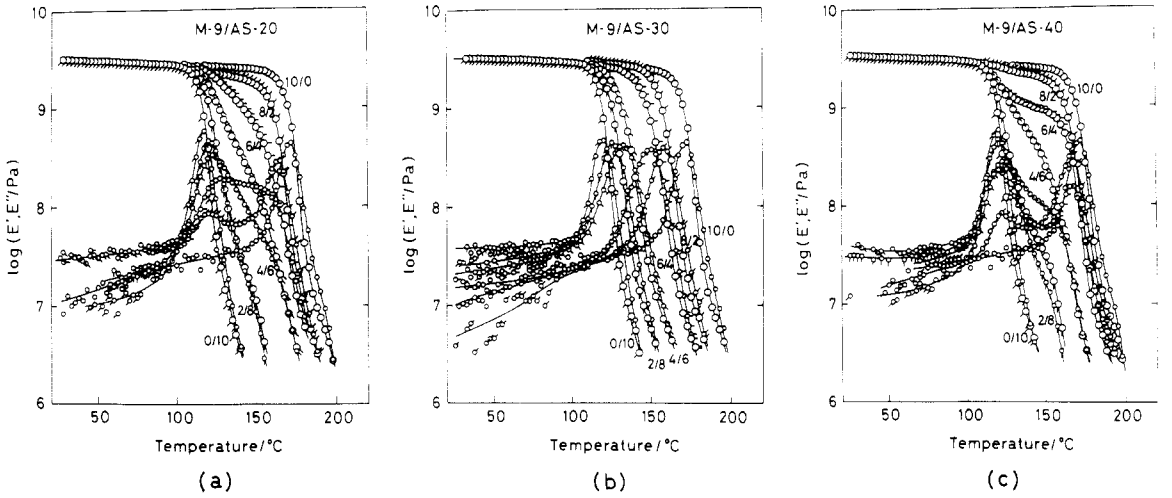

Figure 5. Temperature dispersions of the dynamic storage (E') and loss (E'') moduli at 20 Hz for M-9 blends with AS-20 (a), AS-30 (b), and AS-40 (c).

the two polymers are miscible. For blends of two random copolymers, according to ten Brinke et al.[4] χ_{blend} can be written as a general quadratic equation whose variables are the composition, x and y, of the two copolymers expressed in volume fractions. For blends of the copolymers containing a common monomer unit, $(A_xB_{1-x})_{r_1}$ and $(C_yB_{1-y})r_2$, χ_{blend} is given by

$$\chi_{blend} = \chi_{AB}x^2 + (\chi_{AC} - \chi_{BC} - \chi_{AB})xy + \chi_{BC}y^2 \quad (2)$$

where χ_{AB}, χ_{BC}, and χ_{AC} are the segmental χ parameters between the different monomer units as indicated by their subscripts. Even if all the segmental χ parameters, χ_{AB}, χ_{BC}, and χ_{AC}, are positive, the χ_{blend} can be negative in a limited range of x and y. This happens when χ_{BC} and/or χ_{AB} are larger than χ_{AC}.

Shiomi et al.[6] discussed the theoretical miscibility maps for blends of two random copolymers having a common monomer. Our experimental miscibility maps shown in Figures 6 and 7 can be used to estimate the segmental χ_{ij} parameters for AS/SMA and AS/SPMI blends. Comparing experimental data with theoretical ones by Shiomi et al., it is clear that all the χ_{ij} are positive, because the

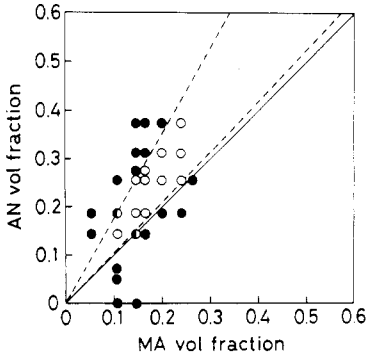

Figure 6. Miscibility regimes for blends of poly(acrylonitrile-*co*-styrene) and poly[styrene-*co*-(maleic anhydride)]: (○) miscible; (●) immiscible; (◐) partially miscible. The broken lines were calculated with $\chi_{AN-MA}/\chi_{AN-S} = 0.04$ and $\chi_{S-MA}/\chi_{AN-S} = 1.89$.

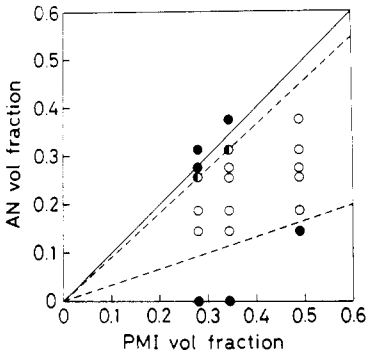

Figure 7. Miscibility regimes for blends of poly(acrylonitrile-*co*-styrene) and poly[styrene-*co*-(*N*-phenylmaleimide)]: (○) miscible; (●) immiscible; (◐) partially miscible. The broken lines were calculated with $\chi_{AN-PMI}/\chi_{AN-S} = 0.07$ and $\chi_{S-PMI}/\chi_{AN-S} = 0.30$.

miscible domains for both blend systems do not contain the line of $x = y$. When $x = y$, χ_{blend} ($=\chi_{AC}y^2$) is positive. Accordingly, the χ_{AC} must be positive.

The boundaries between domains of miscibility and immiscibility were expressed by two straight lines intersecting at the origin, as described before. For AS/SMA blends, two straight lines are given by $(x - 1.8y)(x - 1.05y) = 0$, where x is AN volume fraction and y is MA volume fraction. Comparing the equation with eq 2, we obtain the relations

$$\chi_{AN-MA}/\chi_{AN-S} - \chi_{S-MA}/\chi_{AN-S} - 1 = -2.85$$

$$\chi_{S-MA}/\chi_{AN-S} = 1.85 \times 1.05 = 1.89$$

We can get $\chi_{S-MA}/\chi_{AN-S} = 1.89$ and $\chi_{AN-MA}/\chi_{AN-S} = 0.04$. For AS/SPMI blends, two straight lines are given by $(x - 0.90y)(x - 0.33y) = 0$, where x is the AN volume fraction and y is the PMI volume fraction. We can get $\chi_{S-PMI}/\chi_{AN-S} = 0.30$ and $\chi_{AN-PMI}/\chi_{AN-S} = 0.07$. These results confirm that the so-called repulsion effect can lead to exothermic mixing in the absence of specific interactions.

To determine χ_{ij} we adopted a solubility parameter approach. When there are no specific interactions between the copolymers, χ_{ij} has been expressed as[1,21]

$$\chi_{ij} = (V/RT)(\delta_i - \delta_j)^2 \quad (3)$$

where δ_i and δ_j are the solubility parameters of the respective components and V is a reference volume. V has been taken as the geometric mean of the molar volumes of the involved polymer repeat units, as used by Kressler et al.[22] From group molar constants according to Hoy[23] and the molar volumes by density measurements in this study, the solubility parameters at 23 °C were obtained

Table II
Segmental Interaction Parameters

segment pair	χ_{ij}	segment pair	χ_{ij}
AN–S	0.98	S–MA	1.85
AN–MA	0.04	S–PMI	0.29
AN–PMI	0.07		

$\delta_S = 9.1$, $\delta_{AN} = 12.0$, and $\delta_{MA} = 12.7$ $(cal/cm^3)^{1/2}$. Inserting these values in eq 3, we get for the parameters $\chi_{AN-S} = 0.98$, $\chi_{S-MA} = 1.72$, and $\chi_{AN-MA} = 0.05$. The χ parameter ratios, $\chi_{S-MA}/\chi_{AN-S} = 1.76$ and $\chi_{AN-MA}/\chi_{AN-S} = 0.05$, are in excellent agreement with the values obtained from the miscibility map of AS/SMA blends. By inclusion of $\chi_{AN-S} = 0.98$ into the χ parameter ratios, four segmental interaction parameters were obtained and tabulated in Table II. It is clear that the observed miscibility maps can be explained by the strong repulsions between the segmental units within the copolymers, without any attractive intermolecular interactions.

Concluding Remarks

To estimate segmental interaction parameters, the copolymer compositions should be used in the volume fraction. When the mole or weight fractions are used, incorrect segmental interaction parameters are estimated; e.g., for the AS/SMA blend, even the sign of χ_{AN-MA} is different, although the sign is very important.

The results of this work indicate that AS is miscible with SMA and SPMI within specific ranges of copolymer composition for each blend. The miscibility maps of these copolymer blends could be explained by using the generalized quadratic equation for χ_{blend} derived by ten Brinke et al.[4] Segmental interaction parameters between the different monomer units were estimated. The order of magnitude of the parameters is as follows: $\chi_{S-MA} > \chi_{AN-S} > \chi_{S-PMI} > \chi_{AN-PMI} > \chi_{AN-MA} > 0$. The miscibility of these blends can be explained by strong repulsions between the segmental units within the copolymers.

Registry No. AS, 9003-54-7; SMA, 9011-13-6; SPMI, 26316-43-8.

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special case of $M_1 = M_2$, $V = V_1w_1 + V_2w_2$ (the rule of volume additivity is satisfied). When M_1 is not equal to M_2, the rule of volume additivity is not satisfied. It is caused by a difference of the molecular weights of the comonomers.
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Blend Miscibility of Bisphenol A Polycarbonate and Poly(ethylene terephthalate) As Studied by Solid-State High-Resolution ^{13}C NMR Spectroscopy

P. Mark Henrichs,* John Tribone, and Dennis J. Massa

Corporate Research Laboratories—Eastman Kodak Company, Rochester, New York 14650

James M. Hewitt

Analytical Technology Division—Eastman Kodak Company, Rochester, New York 14650.
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ABSTRACT: Blends of poly(ethylene terephthalate) (PET) and bisphenol A polycarbonate (BPAPC), cast as films from solution in a mixture of hexafluoro-2-propanol and dichloromethane, pressed as a film, and then quenched in ice water, were examined with solid-state high-resolution ^{13}C NMR spectroscopy and differential scanning calorimetry. As prepared, the samples contained separated domains of amorphous PET and BPAPC exceeding 150 Å in size. Heating to 265 °C for about 4 min, followed by cooling in air or in a metal heating block, resulted in crystallization of part of the PET. Further heating and cooling cycles resulted in degradation of the size of the PET crystals while fragments derived from PET were mixed at the molecular level with those derived from BPAPC. The homogenization process apparently occurred as a result of chemical reactions that included the partial loss of the BPAPC carbonyl and a loss of symmetry of the ethylene glycol moiety of PET.

Introduction

Traditional wisdom asserts that polymers of different chemical composition are miscible at the molecular level only in isolated cases. The entropy of mixing that leads to miscibility of many compounds composed of small molecules is essentially absent for high-molecular-weight polymers.

The realization in recent years that, in practice, a great many polymer pairs do form homogeneous blends has stirred considerable interest. The simple fact that the composition of such polymer blends can be varied by the chemist provides a new level of control of polymer properties. Unfortunately, the reasons why some pairs of polymers mix uniformly while other, apparently similar materials, do not is not completely understood. Progress has been made toward development of appropriate theories,[1-7] but additional experimental results on which to base such theories are still needed.

There have been a number of reports that various kinds of polyesters form homogeneous blends with bisphenol A polycarbonate.[8-14] In many cases specific properties of such blends have been measured.[15-21] Thermoplastics containing polyester/polycarbonate blends have a large potential market in automobile parts.

Unfortunately, the early reports that many polyesters are miscible with polycarbonates have not always been supported by later research.[22-24] One complicating factor is the fact that polyesters and polycarbonates can undergo ester–ester interchange reactions, especially at higher temperatures.[24-26] These reactions may lead to apparent miscibility of otherwise incompatible polymers in some cases. Another problem, which is general to the study of all polymer blends, is that the methods used to test polymer miscibility are not always unambiguous. For example, crystallization of one of the polymers during a differential scanning calorimetry scan can obscure one of the glass transitions, leading to the false impression that there is a single glass transition and the polymers are miscible.

NMR spectroscopy is a powerful tool for analysis of the microstructure of solid polymers[27-29] and can help to provide insight about the miscibility of polymer pairs such as a polyester and a polycarbonate. The NMR phenomenon of spin diffusion is an especially fruitful source of information. Spin diffusion is the process by which a perturbation of the spin system at a local site in a solid is dissipated to other sites spatially removed from the site of the initial disturbance. It occurs as a consequence of through-space dipolar interactions among nuclei. Therefore, the nuclei involved must be relatively close to each other in space if spin diffusion is to occur rapidly. Thus spin-diffusion measurements are sensitive to local structure in polymers[30-39] and have been used to check for phase separation in polymer blends in a few cases.[40-43] Another way to view spin diffusion is as a mechanism by which two nuclear reservoirs, prepared with different spin temperatures, can come into equilibrium via the dipolar coupling interactions between the individual nuclei. If each reservoir is associated with one of the components of a polymer blend, the rate at which spin transfer occurs reflects the degree of contact between the components of the polymer blend.

Measurements of spin diffusion have two parts. The spin systems involved must first be prepared with different spin temperatures. That is, the magnetization in at least one of the equilibrating reservoirs must be different from the equilibrium value. The rate at which the spin systems come into equilibrium with each other must then be de-

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