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Viscoelastic Properties of Blends of Poly(acrylonitrile-*co*-styrene) and Poly[styrene-*co*-(*N*-phenylmaleimide)]

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ABSTRACT: Dynamic viscoelastic properties for miscible polymer blends of poly[styrene-*co*-(*N*-phenylmaleimide)] (SMI) and three kinds of poly(acrylonitrile-*co*-styrene)s (AS) with the same composition but different molecular weights (AS-2, AS-3, and AS-4, in increasing molecular weight) are measured by using a concentric cylinder-type rheometer. It is found that the time–temperature superposition principle can be applied over the entire temperature range for the blends. The temperature dependence of the shift factors can be expressed by the WLF equation $\log a_T = -8.86(T - T_s)/(101.6 + T - T_s)$. The T_s and, in other words, the glass transition temperature of the blends increase linearly with an increase in the mole fraction of SMI. The zero-shear viscosities at constant temperatures increase concavely with the SMI content for SMI/AS-2, have a minimum at 20 wt % SMI for SMI/AS-3, and hardly depend on the SMI content for SMI/AS-4. When compared at the same free volume fractions, the zero-shear viscosities decrease convexly with SMI content for all blends. Such compositional dependences of the zero-shear viscosities can be interpreted by the change in the number of entanglement couplings, without any change in each entanglement molecular weight in the component copolymers. It means that the relaxation behavior of the miscible SMI/AS blends is similar to that of a blend consisting of homologous polymers with different molecular weights. It is emphasized that the viscoelastic functions of miscible blends should be compared at the iso-free volume condition.

Introduction

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 the miscibility of the copolymers is due to a repulsion between the two different monomer units comprising the copolymers,[1-3] and in a mean-field approach

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Table I
Styrene Content and Molecular Weight of Copolymers Used

sample	st, wt %	$M_w/10^4$	M_w/M_n
P-30(SMI)	57.7	16.3[a]	1.9
AS-2(AS)	73.7	7.8	2.8
AS-3(AS)	74.9	11.8	2.8
AS-4(AS)	74.3	17.3	2.7

[a] The value was determined by the GPC method calibrated with standard polystyrene.

the overall Flory–Huggins interaction parameter χ between the two polymers can be simply expressed in terms of the respective segmental interaction parameters. ten Brinke et al.[2] extended this formulation to mixtures of two different copolymers. Paul and Barlow[3] and Shiomi et al.[4] applied it to blends of two random copolymers having a common monomer.

Aoki[5] studied miscibility of blends of poly(acrylonitrile-*co*-styrene) (AS) with poly[styrene-*co*-(maleic anhydride)] (SMA) and poly[styrene-*co*-(*N*-phenylmaleimide)] (SMI) and found that ASs are miscible with SMAs and SMIs within specific ranges of copolymer composition for each blend. From the binary interaction model for copolymer mixture, segmental interaction parameters between the different monomer units were estimated and were found to be positive for all pairs. No attractive interactions were found between the acrylonitrile and maleic anhydride or *N*-phenylmaleimide.

Wu[6–8] studied viscoelastic properties of miscible blends of poly(methylmethacrylate) (PMMA) with poly(vinylidene fluoride) (PVDF), poly(ethylene oxide) (PEO), and AS. He discussed the entanglement, friction, and free volume between dissimilar chains in miscible polymer blends in connection with the Flory–Huggins χ parameter. He found that dissimilar chains are less likely to entangle with each other than similar chains. For PMMA/PVDF blend, it results in a large reduction in the zero-shear viscosity in these systems. He also found that the free volume tends to be linearly additive. Inoue et al.[9] investigated orientation relaxation of dissimilar chains in the molten miscible blends PMMA/PVDF and PMMA/poly(vinylidene fluoride-*co*-trifluoroethylene). They suggested that the dissimilar polymers do not relax independently but cooperatively, and this behavior is induced by a constraint due to the specific interactions between the dissimilar chains, e.g., weak hydrogen bonding. Wu[6–8] suggested that, as the interchain interaction becomes stronger, the entanglement probability between dissimilar chains becomes smaller.

As mentioned before, miscible SMI/AS blends have no specific interactions between SMI and AS. In this paper, dynamic viscoelastic properties of miscible SMI/AS blends are measured over wide ranges of temperatures and frequencies by using a concentric cylinder-type rheometer. In order to elucidate the viscoelastic properties of miscible polymer blends without specific interactions between dissimilar chains, compositional dependences of the shift factors and zero-shear viscosities are studied. The results are discussed in terms of the free volume concept and entanglement coupling.

Experimental Section

A SMI and three ASs with the same composition but different molecular weights were prepared by radical polymerization. Table I shows the composition and molecular weight of these copolymers used in this study. Acrylonitrile content of AS and *N*-phenylmaleimide content of SMI were measured by elementary analysis (Yanaco, CHN coder). The weight-average molecular weight (M_w) of the AS samples was determined by low-angle laser light scattering (Chromatix, KMX-6) and the polydispersity index M_w/M_n by GPC (Waters Associates, ALC/GPC Model 150C) using tetrahydrofuran as the solvent. M_w and M_w/M_n of the SMI sample were determined by the GPC method calibrated with standard polystyrene.

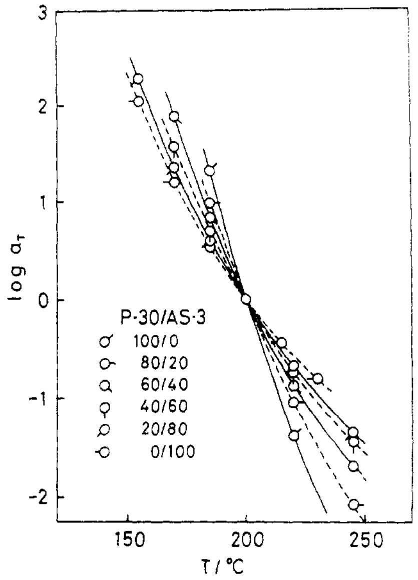

Figure 1. Temperature dependence of the shift factors a_T for the P-30/AS-3 blends at the reference temperature of 200 °C.

SMI/AS blends of various composition ratios were prepared by melt extrusion. The blend composition ratios were SMI/AS = 0/100, 20/80, 40/60, 60/40, 80/20, and 100/0 by weight. All the blends were transparent. Miscibility of these blends was also determined by measuring their glass transition temperatures with dynamic mechanical testing. It was found that the temperature dispersion curves for the loss modulus E'' have a single peak and the E'' peaks exist at a temperature intermediate between those of the respective pure components. These are evidence for the miscibility of these blends.

A concentric cylinder-type rheometer (Thixotrometer, Iwamoto Seisakusho Co.) was used for measurements of viscoelastic properties of the samples. The measuring temperatures were varied from 140 to 245 °C and the frequencies from 6.67×10^{-4} to 1.0 Hz. The frequency-dependence curves of the storage shear modulus G' and the loss modulus G'' at various temperatures were superimposed onto the master curves at 200 °C according to the time–temperature superposition. All measurements were performed under nitrogen so as to minimize oxidative degradation at high temperature.

Results and Discussion

Figure 1 shows the temperature dependence of the shift factors a_T for the P-30/AS-3 blends. The reference temperature is 200 °C for all the samples. The temperature dependence of a_T becomes steep with an increase in the P-30 content. But, when the reference temperatures were chosen at 136, 145, 155, 166, 181, and 198 °C for P-30/AS-3 = 0/100, 20/80, 40/60, 60/40, 80/20, and 100/0, all the curves could be expressed in a single WLF equation[10] denoted by the dotted line in Figure 2

$$\log a_T = -c_1(T - T_s)/(c_2 + T - T_s) \qquad (1)$$

where T is the temperature, T_s is the reference temperature, $c_1 = 8.86$, and $c_2 = 101.6$. Figure 3 shows the compositional dependence of T_s for the P-30/AS-3 blends. T_s of the blends was found to be a linear function of the mole fraction x of SMI, just the same as that for SMA/AS blends found previously by us.[11] Accordingly, T_s^{blend} is given by

$$T_s^{\text{blend}} = (1 - x)T_s^{\text{AS}} + xT_s^{\text{SMI}} \qquad (2)$$

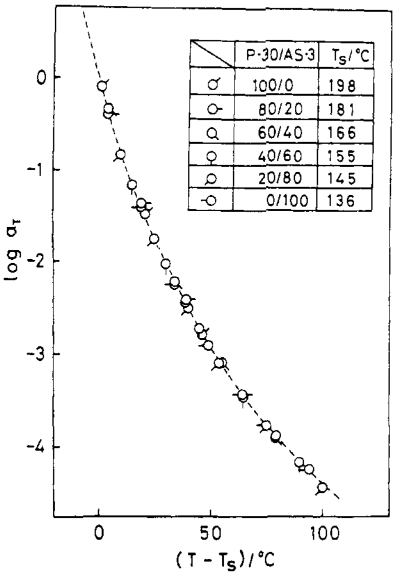

Figure 2. Temperature dependence of the shift factors a_T for the P-30/AS-3 blends. The reference temperatures are shown in the figure.

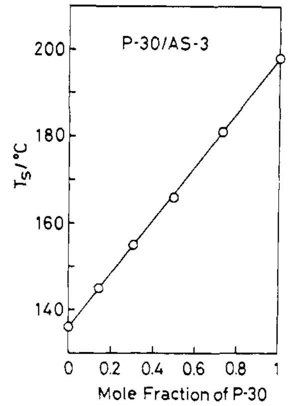

Figure 3. Compositional dependence of the reference temperature T_s for the P-30/AS-3 blends.

where T_s^{AS} is the T_s of AS and T_s^{SMI} that of SMI. It is said that the T_s expressed by eq 1 is 50 °C higher than the glass transition temperature T_g for many polymers.[10] Equation 2 implies that the glass transition temperature of the SMI/AS blends is a linear function of the mole fraction of SMI. For the P-30/AS-2 and P-30/AS-4 blends, eqs 1 and 2 were found to be applicable.

The above data can be understood in terms of the free volume concept and the additivity of the free volumes of the component copolymers. The free volume of a polymer, f, at a temperature T_s is given by

$$f = f_0 + \alpha(T - T_s) \tag{3}$$

where f_0 is the free volume at T_s and α the temperature coefficient of that free volume. According to the Doolittle equation[12] which describes the relationship between the viscosity of a system and the temperature dependence of the free volume, f_0 is $B/2.303c_1$ and α is f_0/c_2, where B is a constant of the order of 1. The results in Figure 2 indicate that both c_1 and c_2 are constant at each T_s shown in Table II for the component copolymers and blends. Accordingly, f_0 and α are also constant at each T_s independent of composition. The free volume of blends, f^{blend}, is given by

$$f^{\text{blend}} = f_0 + \alpha(T - T_s^{\text{blend}}) \tag{4}$$

Table II
Reference Temperatures T_s (°C) of Various SMI/AS Blends

	blend ratio					
sample	0/100	20/80	40/60	60/40	80/20	100/0
P-30/AS-2	134	144	154	166	180	198
P-30/AS-3	136	146	155	166	181	198
P-30/AS-4	137	145	155	166	181	198

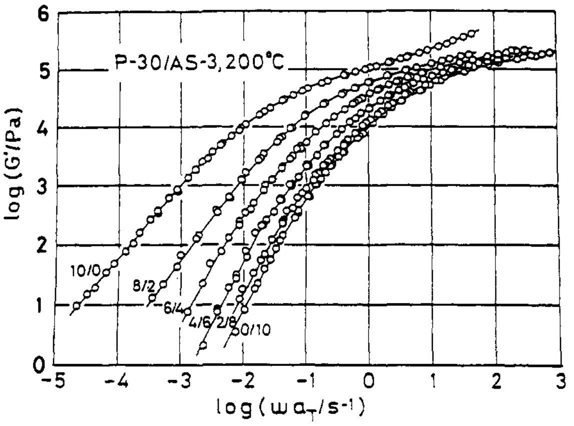

Figure 4. Master curves of the storage shear modulus G' reduced to 200 °C for the P-30/AS-3 blends.

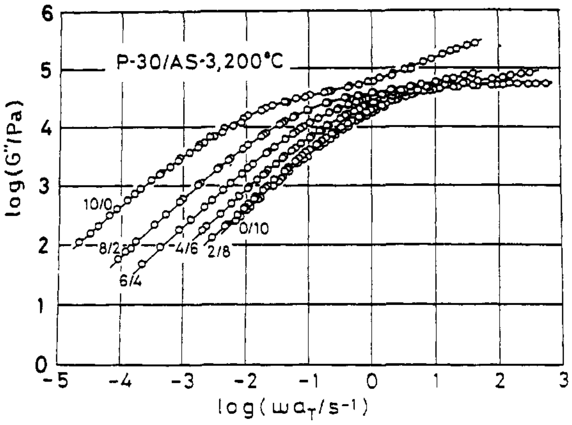

Figure 5. Master curves of the loss shear modulus G'' reduced to 200 °C for the P-30/AS-3 blends.

Putting eq 2 into eq 4

$$f^{\text{blend}} = (1 - x)f^{\text{AS}} + xf^{\text{SMI}} \tag{5}$$

Equation 5 indicates that the additivity of the free volumes of the component copolymers is applicable for the SMI/AS blends. In other words, AS (low T_g component) may be considered as a diluent for SMI (high T_g component). Wu[7] also found that the free volume of the miscible blends tend to be linearly additive.

Figures 4 and 5 show the master curves of G' and G'' for the P-30/AS-3 blends and the component copolymers, respectively, as a function of the reduced angular frequency ωa_T. At high frequencies, the heights of G' and G'' are constant and independent of the blend ratio. At low frequencies, G'' is proportional to ωa_T for each sample. This is a Newtonian flow region where the dynamic viscosity $\eta' = G''/\omega$ is independent of the frequency. Therefore, the zero-shear viscosity ($\eta_0 = \lim_{\omega a_T \to 0} \eta'$) can be calculated from these data.

Figure 6 shows the compositional dependence of the zero-shear viscosity η_0 at 200, 220, and 245 °C. For the P-30/AS-2 blends, η_0 increases concavely with an increase in weight fraction of P-30. For the P-30/AS-3 blends,

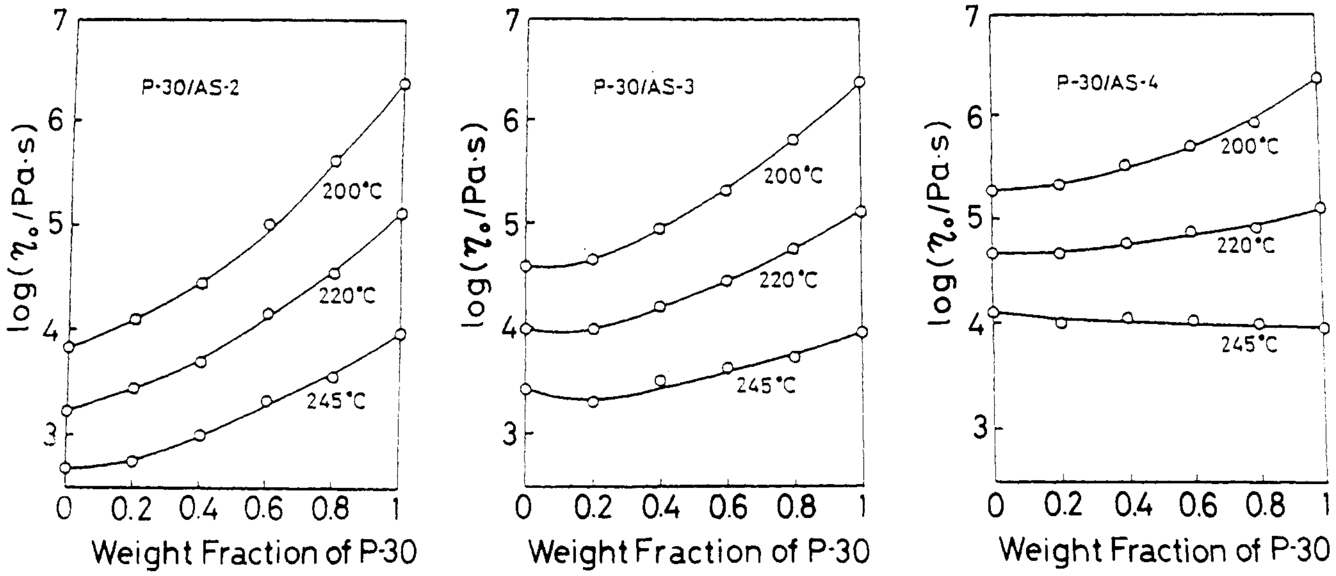

Figure 6. Compositional dependence of the zero-shear viscosity η_0 for the P-30/AS-2, P-30/AS-3, and P-30/AS-4 blends at constant temperatures.

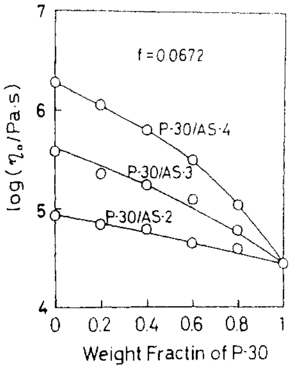

Figure 7. Compositional dependence of the zero-shear viscosity η_0 for the P-30/AS-2, P-30/AS-3, and P-30/AS-4 blends at $f = 0.0672$.

the η_0 has minima at about 20 wt % P-30 and then increases with increasing weight fraction of P-30. For the P-30/AS-4 blends, the compositional dependence of η_0 is very small because the difference between the η_0 of P-30 and that of AS-4 is small. The existence of the minima found for the P-30/AS-3 blends seems to support Wu's explanation that dissimilar chains are less likely to entangle with each other than similar chains.[6-8] However, as shown in Figure 6, compositional dependences of η_0 are varied by measuring temperature. This fact implies that η_0 behavior is affected by a free volume in the blends. Compositional dependences of η_0 at a constant free volume fraction of 0.0672 are plotted in Figure 7. η_0 decreases convexly with an increase in P-30 content. This result reminds us of the viscoelastic properties of the blends of homologous polymers with different molecular weights.

The molecular weight dependence of η_0 of AS at a constant free volume fraction was expressed by $\eta_0 = K(M_w/M_e)^{3.8}$. Using the entanglement molecular weight of AS, M_e(AS) = 11 000, evaluated by Wu,[7,8] the number of entanglements, $n_w = M_w/M_e$, is estimated to be 7.1, 10.7, and 15.7 for AS-2, AS-3, and AS-4, respectively. Assuming that constant K of SMI is the same as that of AS, n_w of P-30 is 5.3. When the entanglement molecular weights in the blends are identical with those in the component copolymers, the number of entanglements in the blend, n_w^{blend}, can be expressed by

$$n_w^{\text{blend}} = w_1 n_w^{\text{SMI}} + w_2 n_w^{\text{AS}} \qquad (6)$$

where w_1 is the weight fraction of SMI and w_2 that of AS. Using eq 6, η_0 was calculated and plotted by solid lines in Figure 7. The calculated curves are in good agreement with experimental values. These results suggest that the dissimilar polymers relax independently and entanglement molecular weights in the blends are the same as those in each component copolymer. Wu[6-8] calculated the M_ws for the blends by $M_w = w_1 M_{w1} + w_2 M_{w2}$. But, we believe that the above relation is meaningless and eq 6 should be used instead of the additivity of the molecular weights.

Concluding Remarks

The viscoelastic properties of miscible SMI/AS blends, which have no specific interactions between dissimilar chains, are investigated. The additivity of the free volumes of the component copolymers is applicable for SMI/AS blends. The zero-shear viscosity of the blends exhibits a behavior similar to that of a blend consisting of homologous polymers with different molecular weights. It is emphasized that the rheological behavior of miscible blends should be compared at an iso-free volume condition and that the entanglement molecular weights in the miscible blends are identical with those in the component copolymers.

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