Viscoelastic Properties of Miscible Poly(methyl methacrylate)/Poly(styrene-*co*-acrylonitrile) Blends in the Molten State

Yuji Aoki*

Chemical Science Laboratories, Mitsubishi Chemical Corporation, 1, Toho-cho, Yokkaichi, Mie 510-8530, Japan

Takeshi Tanaka

ACT Research Center Inc., 3-3-7, Obata, Yokkaichi, Mie 510-0875, Japan

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ABSTRACT: Dynamic viscoelastic properties for three kinds of miscible blends of poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-acrylonitrile) (SAN) have been measured. 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 increases linearly with an increase in the weight fraction of PMMA. The zero-shear viscosity versus blend composition curves deviate positively from linear additivity for the blends at both constant temperature and free volume fraction. The plateau modulus, determined as the storage modulus G' in the plateau zone at the frequency where $\tan \delta$ is at a minimum, varies linearly with blend composition for the PMMA-7 ($M_w = 7.2 \times 10^4$)/SAN-18 ($M_w = 11.6 \times 10^4$, AN = 18.4 wt %) and PMMA-7/SAN-27 ($M_w = 8.4 \times 10^4$, AN = 27.0 wt %) blends, but concavely with the blend composition for the PMMA-60 ($M_w = 59.3 \times 10^4$)/SAN-18 blends. It is considered that the above method to determine the plateau modulus cannot be applicable for the PMMA-60/SAN-18 blends, because of the great difference in the concentration of entanglements. It is concluded that the relaxation behavior of the PMMA/SAN blends is similar to that of a blend consisting of homologous polymers, and the entanglement molecular weights in PMMA/SAN blends are identical with those in the component polymers.

Introduction

About a decade ago, Wu[1−3] studied viscoelastic properties of several miscible blends including poly(methyl methacrylate) (PMMA) with poly(vinylidene fluoride) (PVDF), poly(ethylene oxide) (PEO), and poly(styrene-*co*-acrylonitrile) (SAN). He analyzed compositional dependence of the plateau modulus and zero-shear viscosity and reported that, due to specific interchain interactions, dissimilar chains are less likely to entangle than similar chains. He discussed the entanglement, friction, and free volume between dissimilar chains in miscible polymer blends in connection with the Flory−Huggins χ parameter. He suggested that, as the interchain interaction becomes stronger, the entanglement probability between dissimilar chains becomes smaller.

Han and Kim[4,5] developed a molecular theory to predict the linear viscoelastic properties of binary mixtures of miscible blends, using the concept of the tube model of Doi and Edwards.[6] They assumed that each primitive chain reptates in a respective tube but that molecular interactions between the two chemically dissimilar primitive chains take place under the influence of an external potential, dependent upon the interaction parameter of the constituent components. Their theory predicts the following: (1) When the viscosity ratio η_{01}/η_{02} of the constitutive components is much greater than 1, the log η_{0b} versus blend composition curves show negative deviation from linearity for $\chi < 0$ and positive deviations for $\chi \approx 0$. (2) When the η_{01}/η_{02} ratio is close to 1, the value of log η_{0b} has a minimum at a certain blend composition for $\chi < 0$. They found that the predicted behavior of log η_{0b} versus blend composition (positive deviation) is agreement with experimental data for PMMA/SAN blends of the nearly zero value of χ.

We studied viscoelastic properties of miscible blends of poly[styrene-*co*-(*N*-phenylmaleimide)] (SMI) and three kinds of SAN.[7] We found that the log η_{0b} versus blend composition curves show negative deviation at constant temperature but show positive deviation at an iso-free volume fraction. 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 viscoelastic behavior of the miscible SMI/SAN blends is similar to that of a blend consisting of homologous polymers with different molecular weight.

On the other hand, Watanabe et al.[8] and Doi and Watanabe[9] formulated the dynamics of Rouse chains that interact with each other with a nematic potential. They concluded that the rheological properties on the long time scale are very *insensitive* to the nematic interaction, that is, an interaction between the segments of the chain and matrix. This conclusion indicates that interchain specific interactions responsible for the miscibility do not influence the rheological properties on the long time scale, such as the plateau modulus and zero-shear viscosity of miscible polymer blends.

Colby[10] reported that the time−temperature superposition principle failed for miscible PMMA/PEO blend in the terminal region. Ngai and Plazek[11] explained his results using the coupling theory. Very recently, during

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* To whom all correspondence should be addressed. E-mail 1102000@cc.m-kagaku.co.jp.

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Table 1. Molecular Characteristics of the Samples

polymer	M_w	M_w/M_n	AN wt %	st	ht	it
PMMA-7	72 000	1.7		57.0	38.1	4.9
PMMA-60	593 000	3.2		49.2	40.3	10.5
SAN-18	116 000	2.1	18.4			
SAN-27	84 000	2.4	27.0			

our preparing this paper, Pathak et al.[12] reported the linear viscoelasticity of miscible PMMA/SAN blends in detail. They found that the blends are thermorheologically simple, and these results are anticipated by a theory of concentration-fluctuation-induced dynamic heterogeneity[13] in miscible polymer blends.

It is very interesting know whether specific interchain interactions of miscible blends change the entanglement concentration between dissimilar chains in the academic field. On the other hand, it is very important to know the exact value of χ parameter in order to develop new polymer blends in the industrial field, if the conclusions by Wu are true. In this paper, we measure dynamic viscoelastic properties of three kinds of miscible PMMA/SAN blends over wide range of temperatures and frequencies and elucidate the viscoelastic properties of miscible polymer blends, compositional dependences of the shift factor, zero-shear viscosity, and plateau modulus. We report that the χ parameter does not affect linear viscoelastic properties for miscible blends with weak energetic interactions and explain why incorrect conclusions were drawn.

Experimental Section

Materials. Two PMMA samples were used in this study. One (PMMA-7) was obtained commercially and the other (PMMA-60) from Scientific Polymer Products, Inc. SAN samples were prepared by radical polymerization. Table 1 shows the tacticity (PMMA) or composition (SAN) and molecular weight of these polymers. The tacticity of PMMA was determined by ^{1}H NMR (JEOL, EX-270) using chloroform-*d* as solvent. The amounts of syndiotactic (st), heterotactic (ht), and isotactic (it) triads were determined by integrating over peaks at 0.85, 1.02, and 1.21 ppm, respectively. The AN content of SAN was measured by elementary analysis (Yanaco, CHN coder). The weight-average molecular weight (M_w) of the samples was determined by light scattering (Otsuka Electronics, DLS-700) and polydispersity index M_w/M_n by GPC (Waters Associates, ALC/GPC model 150C) using tetrahydrofuran (THF) as solvent.

Three series of PMMA/SAN blends (PMMA-7/SAN-18, PMMA-7/SAN-27, and PMMA-60/SAN-18) were prepared by casting films from THF solutions (5 wt %) at room temperature. The films were then dried thoroughly in a vacuum oven at 320−383 K for 2−3 days. The blend composition ratios were PMMA/SAN = 0/100, 20/80, 40/60, 50/50, 60/40, 80/20, and 100/0 by weight. The reasons why we selected the above three series of PMMA/SAN blends are as follows. Before starting the viscoelastic study, we checked the miscibility of PMMA-7 and SANs with various AN percents. Miscibility was observed in these blends for SAN with AN content between 10 and 27 wt %. Therefore, the χ parameter of PMMA-7/SAN-18 blends must be the smallest among the PMMA-7/SAN blends, and PMMA-7/SAN-27 blends are a margin of miscibility, although we do not know the precise values of χ parameters. PMMA-60/SAN-18 blends were selected to study the effects of molecular weight.

The glass transition temperatures of the component polymers and their blends were determined by differential scanning calorimeter on a Perkin-Elmer DSC-7 with about 10 mg of sample. Heating rate was 20 K/min. Two T_g values—$T_g(1)$ is the onset temperature and $T_g(2)$ the midpoint temperature of the transition during the second heating—were obtained.

Viscoelastic Measurements. Viscoelastic measurements were carried out with a Rheometrics ARES-2KFRTN1 with parallel-plate geometry (25 mm diameter plates and 1−2 mm gap heights). The storage modulus (G') and loss modulus (G'') were measured as a function of frequency (ω). Measurements were taken at different temperatures in order to investigate the temperature dependence of the viscoelastic properties. The frequency dependence curves of G' and 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

Temperature Dependence of Shift Factor a_T of PMMA/SAN Blends. Figure 1a shows the temperature dependence of the shift factor a_T for the PMMA-7/SAN-18 blends. The reference temperature is 200 °C for all the blends. The temperature dependence of a_T becomes slightly steep with an increase in PMMA content, as the T_g increases. But, when the reference temperatures T_s were chosen at 138, 141, 144, 146, 149, and 152 °C for PMMA-7/SAN-18 = 0/100, 20/80, 40/60, 60/40, 80/20, and 100/0, all the curves could be expressed in a single WLF equation denoted by the dotted line in Figure 1b

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

where T is the temperature, T_s is the reference temperature, $c_1 = 8.86$, and $c_2 = 101.6$. Provided that data are taken over a sufficiently wide temperature range, this procedure determines T_s to within ±1 K.

Figure 2 shows the compositional dependence of T_s for the PMMA-7/SAN-18 blends. T_s of the blends was found to be a linear function of the weight fraction (x) of PMMA. Accordingly, $T_s^{\rm blend}$ is given by

$$T_s^{\rm blend} = (1 - x)T_s^{\rm SAN} + xT_s^{\rm PMMA} \quad (2)$$

where $T_s^{\rm SAN}$ is the T_s of SAN and $T_s^{\rm PMMA}$ that of PMMA. Equation 2 can be rewritten to the additivity of the free volumes of the component polymers as described by the previous paper.[7]

$$f^{\rm blend} = (1 - x)f^{\rm SAN} + xf^{\rm PMMA} \quad (3)$$

where $f^{\rm blend}$, $f^{\rm SAN}$, and $f^{\rm PMMA}$ are the free volume of the blend, SAN, and PMMA at constant temperature.

Pathak et al.[12] studied the temperature dependence of the shift factor a_T for PMMA/SAN blends in detail. They evaluated WLF coefficients by plotting log a_T versus $(T - T_g)/(T - T_\infty)$ using the Vogel temperature T_∞ as a free parameter to linearize the plot according to Plazek[14] and reported this procedure to be the most objective and reliable. Figure 3 shows the composition dependence of $T_g(1)$ and $T_g(2)$ of the PMMA-7/SAN-18 blends, where $T_g(1)$ is the onset temperature and $T_g(2)$ the midpoint temperature of the glass transition. As expected, both the glass transition temperatures are a linear function of the PMMA content. Difference between $T_g(1)$ and $T_g(2)$ is about 20 °C and depends slightly on the blend composition. The accuracy of the midpoint temperature $T_g(2)$ is much better than that of the measurement of the onset temperature $T_g(1)$. Reproducibility in $T_g(2)$ results in ±0.5 K error, but the error in the measurement of $T_g(1)$ is much larger, resulting in larger than ±2 K. We think that $T_g(1)$ is a

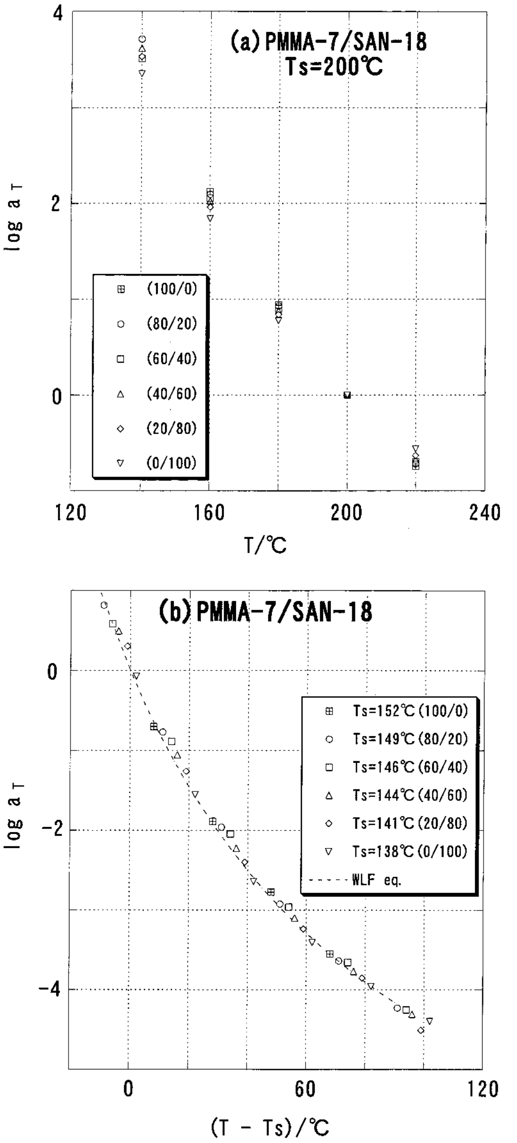

Figure 1. Temperature dependence of the shift factor a_T at 200 °C (a) and T_s indicated in the figure (b) as a function of temperature for the PMMA-7/SAN-18 blends.

value near to “real” T_g determined on dilatometry. The Vogel temperature T_∞ obtained from the above method depends strongly on the T_g value used, although they used T_g as the midpoint of DSC curves. Therefore, we like to utilize T_s as an adjustable parameter.

PMMA-7/SAN-27 and PMMA-60/SAN-18 blends were also thermorheologically simple. The reasons may be due to dynamic symmetry of PMMA and SAN, as already explained by Pathak et al.[12] The temperature dependence of a_T for these blends is essentially same as that for the PMMA-7/SAN-18 blends, although we do not show them.

Master Curves and Zero-Shear Viscosity η_0 of PMMA/SAN Blends. Parts a and b of Figure 4 show the master curves of G' and tan δ and G'' for the PMMA-7/SAN-18 blends and the component polymers, respectively, as a function of the reduced angular frequency ωa_T at reference temperature of 200 °C. They show the terminal zone at low frequencies, the plateau zone at intermediate frequencies, and entry into the transition zone at higher frequencies. At low frequencies, G' is proportional to $(\omega a_T)^2$ and G'' to ωa_T for each sample. In the terminal zone the dynamic viscosity $\eta' = G''/\omega$ is independent of frequency. Therefore, the zero-shear viscosity ($\eta_0 = \lim_{\omega a_T \to 0} \eta'$) can be calculated from these data. The terminal relaxations of PMMA-7 and SAN-18 are too close to resolve cleanly. Parts a and b of Figure 5 show the master curves of G' and tan δ and G'' for the PMMA-60/SAN-18 blends and the component polymers, respectively, as a function of the reduced angular frequency ωa_T. It is observed that the rubbery plateau zone of PMMA-60 is wider than that of PMMA-7.

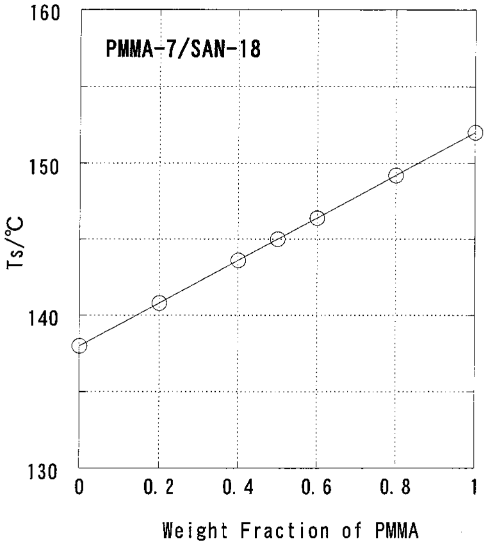

Figure 2. Compositional dependence of the reference temperature T_s for the PMMA-7/SAN-18 blends.

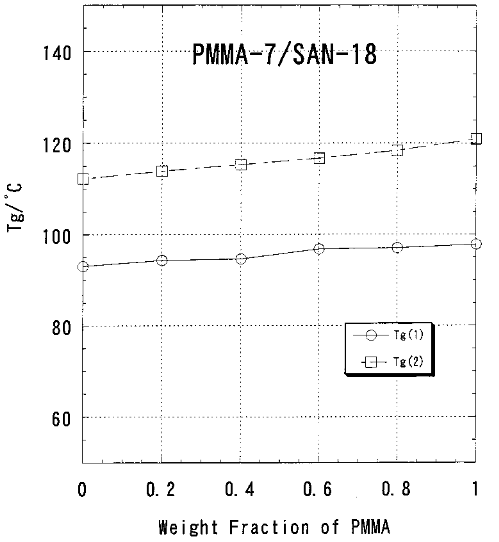

Figure 3. Compositional dependence of the onset temperature $T_g(1)$ and the midpoint temperature $T_g(2)$ of the glass transition for the PMMA-7/SAN-18 blends.

Figure 6a,b shows the compositional dependence of the zero-shear viscosity η_0 at 200 °C and $f = 0.049$. Both the η_0 versus PMMA content curves deviate positively from additivity for both polymers. These experimental results are qualitatively agreement with the results by Wu[3] and by Han and Kim.[4,5] Wu proposed that the zero-shear viscosity η_0 of miscible blends is expressed by eq 4.[2]

$$\log \eta_0 = \phi_1 \log \eta_{01} + \phi_2 \log \eta_{02} + \phi_1\phi_2 \log \lambda \quad (4)$$

where η_{0j} and ϕ_j are the zero-shear viscosity and the

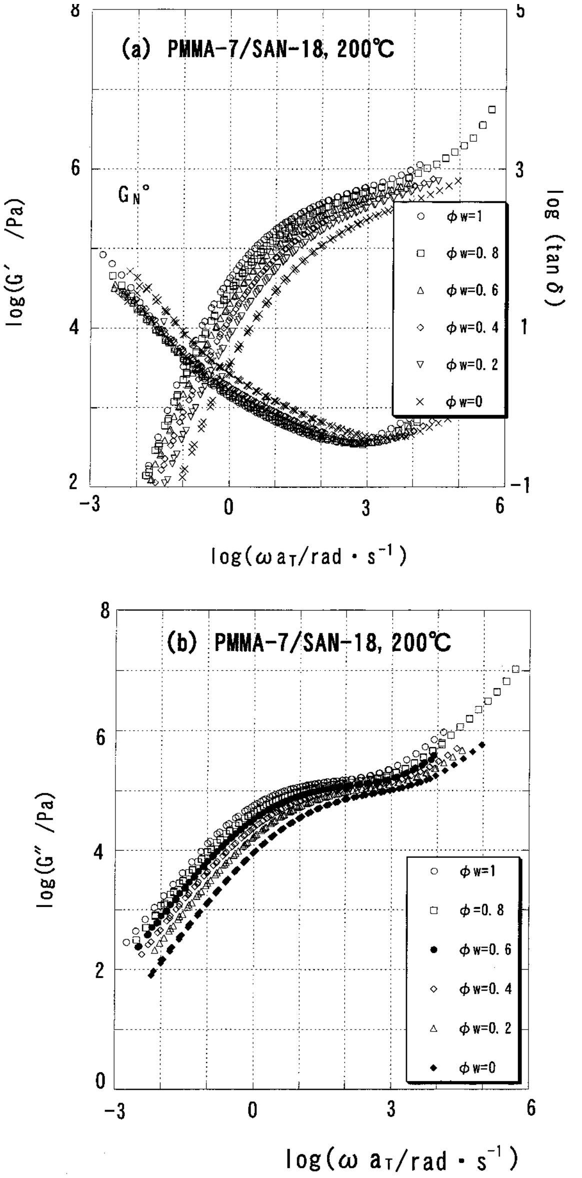

Figure 4. Master curves of the storage modulus G' and loss tangent tan δ (a) and loss modulus G'' (b) reduced to 200 °C for the PMMA-7/SAN-18 blends.

volume fraction of pure component j, respectively, and λ is a constant for a blend system. Wu[3] reported that the zero-shear viscosity of PMMA/SAN blends at 180 °C shows a positive deviation from linearity. But, he compared the η_0 at the same molecular weight and obtained log $\lambda = 0$. He stated that log $\lambda = 0$ is not expected to be generally applicable to other miscible blends. Our data exhibit positive deviation from linearity, which are different from Wu's data, and fit well to log $\lambda = 0.3$, as shown in Figure 6b. We can interpret our data as follows.

Previously, we proposed that the rheological behavior of miscible blends should be compared at an iso-free volume condition.[7] Assuming the additivity of the number of entanglements (n_{wj}) in the blends instead of the additivity of the molecular weight,

$$n_w^{\mathrm{blend}} = \omega_1 n_{w1} + \omega_2 n_{w2} \qquad (5)$$

where ω_1 is the weight fraction of component 1 and ω_2 that of component 2, we have found that the calculated curves are in good agreement with experimental values of SMI/SAN blends at an iso-free volume fraction. We applied the above proposal to PMMA/SAN blends. Using eq 5, the η_0 values of the PMMA-7/SAN-18 were calculated according to the method of the previous paper. The calculated values are very similar to the solid line (log $\lambda = 0.3$ of eq 4) in Figure 6b and are in good agreement with experimental ones. These findings are convincing evidence that the zero-shear viscosity of PMMA/SAN blends is similar to that of a blend consisting of homologous polymers with different molecular weight, as reported for SMI/SAN blends previously by us.[7]

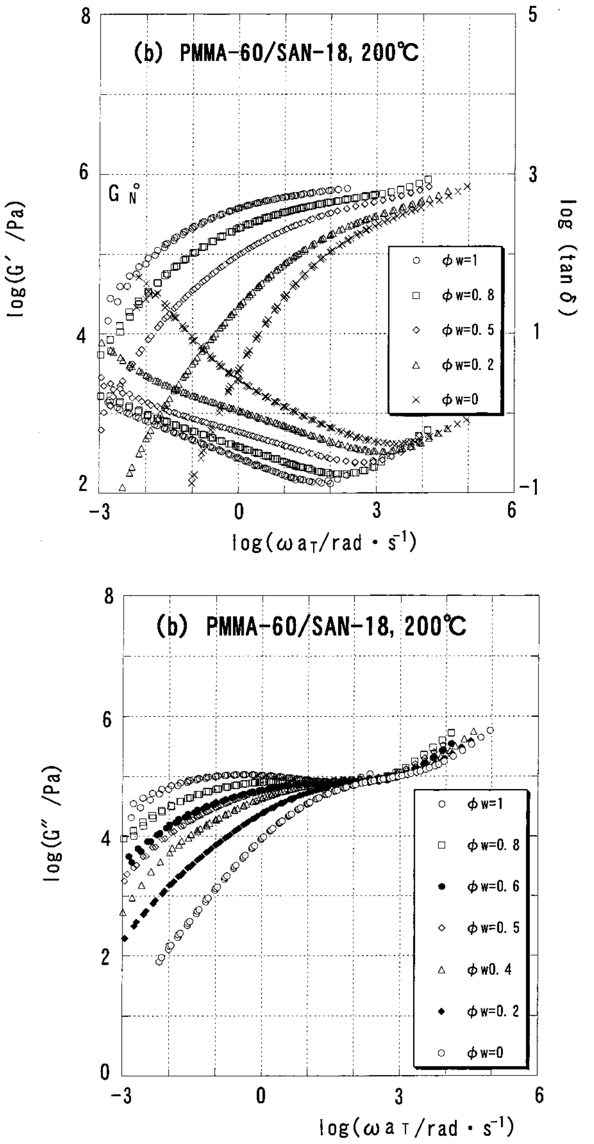

Figure 5. Master curves of the storage modulus G' and loss tangent tan δ (a) and loss modulus G'' (b) reduced to 200 °C for the PMMA-60/SAN-18 blends.

Plateau Modulus G_N^0 of PMMA/SAN Blends. The plateau modulus G_N^0 was determined as the storage modulus G' in the plateau zone at the frequency where tan δ is at a minimum. The G_N^0 values were obtained from the master curves shown in Figures 4a and 5a. Parts a, b, and c of Figure 7 show the plateau modulus versus the volume fraction, ϕ_1, of PMMA for the PMMA-7/SAN-18, PMMA-7/SAN-27, and PMMA-60/SAN-18, respectively. The G_N^0 shows a linear function of ϕ_1 for the PMMA-7/SAN-18 and PMMA-7/SAN-27 blends but shows a negative deviation from linearity for the

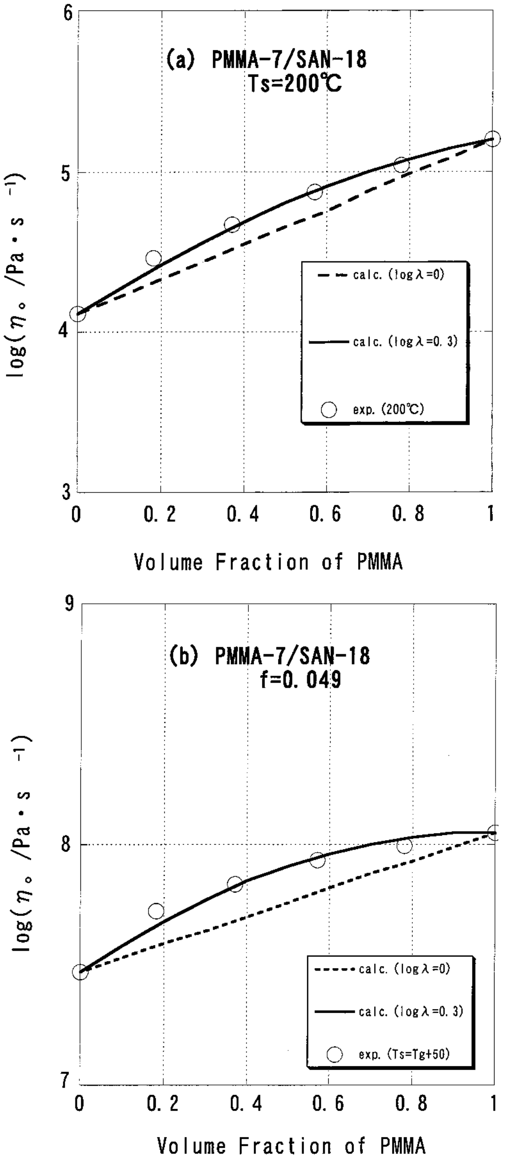

Figure 6. Compositional dependence of the zero-shear viscosity η_0 for the PMMA-7/SAN-18 blends at 200 °C (a) and $f = 0.049$ (b).

PMMA-60/SAN-18 blends.

Wu[1−3] proposed that the plateau modulus $G_N{}^0$ of miscible blends is expressed by eq 6,

$$G_N{}^0 = \phi_1 G_{N1}{}^0 + \phi_2 G_{N2}{}^0 + \phi_1\phi_2(\lambda_e - 1)(G_{N1}{}^0 + G_{N2}{}^0) \tag{6}$$

where ϕ_j and $G_{Nj}{}^0$ are the volume fraction and plateau modulus of component j, respectively, assuming binary interaction contacts with constant probability of entanglement for each type of contact. The λ_e is a constant for a given system, given by

$$\lambda_e = [(\rho_1\rho_2)^{1/2}/M_{e12}]/[(1/2)(\rho_1/M_{e1} + \rho_2/M_{e2}) \tag{7}$$

The M_{e12} is the entanglement molecular weight of a hypothetical pure component having a density $(\rho_1\rho_2)^{1/2}$ and the same entanglement probability as that between dissimilar chains in the real blend. Figure 7a,b indicates that $\lambda_e = 1.0$ for the PMMA-7/SAN-18 and PMMA-7/SAN-27 blends. It means that entanglement molecular weights in these blends are same as those in each component polymer independent of χ parameter. On the other hand, λ_e of PMMA-60/SAN-18 blend is in agreement with Wu's result of 0.775.

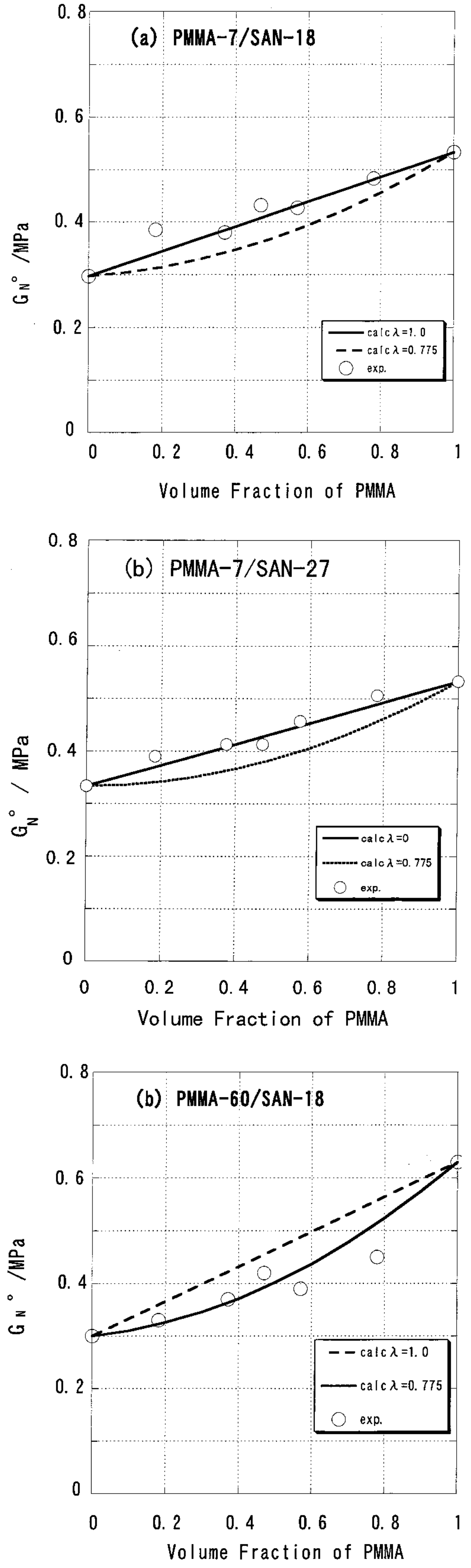

Figure 7. Compositional dependence of the plateau modulus $G_N{}^0$ for the PMMA-7/SAN-18 (a), PMMA-7/SAN-27 (b), and PMMA-60/SAN-18 (c) blends.

Table 2. Entanglement Molecular Weight M_e and Number of Entanglement n_e for PMMA-7, PMMA-60, SAN-18, and SAN-27

polymer	M_w	M_e	n_e
PMMA-7	72 000	7 980	9.0
PMMA-60	593 000	6 840	87
SAN-18	116 000	12 800	9.1
SAN-27	84 000	11 520	7.3

Let's consider the reason for the discrepancy of λ_e for PMMA/SAN blends. First, we calculated the entanglement molecular weight M_e between entanglement points for SAN-18, SAN-27, PMMA-7, and PMMA-60 by

$$M_e = \rho RT/G_N^0 \tag{8}$$

where ρ is the density and R the gas constant. Table 2 shows M_e and the number of entanglement n_e for SAN-18, SAN-27, PMMA-7, and PMMA-60. Next, we compare parts a and b of Figure 4. Master curves of G' and tan δ of the PMMA-7/SAN-18 blends are very similar for each blend composition, because the number of entanglement couplings of each polymer is almost same. The tan δ values at minimum were 0.36−0.41, almost independent of the composition. On the other hand, tan δ curves of the PMMA-60/SAN-18 blends are skewed, and the tan δ values at minimum were 0.13−0.41, dependent on the composition. Such behavior is similar to that of a blend consisting of homologous polymers with different molecular weight. An extreme case is a blend of two homologous polymers with narrow molecular weight distribution. In this case, we cannot determine the plateau modulus from the storage modulus at the frequency where tan δ is a minimum. For the PMMA-60/SAN-18 blends, the difference in the number of entanglement couplings is very large. Therefore, the above method to determine the plateau modulus would not be applicable to the PMMA-60/SAN-18 blends. Wu and Beckerbauer[15] reported that G_N^0 determined by the above method is invariant with respect to molecular-weight and molecular-weight distribution and is equal to the G_N^0 value determined by the integration of the G'' curve. However, M_w/M_n of their samples is within about 4, although the ratio of n_e for the PMMA-60/SAN-18 blends is about 10. Our data indicate that the plateau modulus of PMMA/SAN blends is a linear function of blend composition.

Wu[1−3] proposed that specific interchain interactions, responsible for miscibility of dissimilar polymers, tend locally to align the chain segments for association and thus stiffen the chains, resulting in reduced entanglement between dissimilar chains. This local ordering can be regarded as a kind of nematic interaction. Watanabe et al.[8] and Doi and Watanabe[9] formulated the dynamics of Rouse chains that interact with each other by nematic potential. They concluded that the rheological properties on the long time scale are very insensitive to the nematic interaction, an interaction between the segments of the chain and matrix. This conclusion indicates that interchain specific interactions responsible for the miscibility do not influence the rheological properties on the long time scale such as the plateau modulus and zero-shear viscosity of miscible blends and supports our experimental results.

Conclusions

Dynamic viscoelastic properties of PMMA/SAN blends were measured. It was found that the plateau modulus varies linearly, and the zero-shear viscosity deviates positively with blend composition. It was concluded that the entanglement molecular weights in PMMA/SAN blends are identical with those in the component polymers. The specific interaction in miscible blends, in other words, χ parameter, does not change the rheological properties on the long time scale.

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