Melt Rheology of Poly(ϵ-caprolactone)/Poly(styrene-*co*-acrylonitrile) Blends

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ABSTRACT: Dynamic viscoelastic properties for miscible blends of poly(ϵ-caprolactone) (PCL) and poly(styrene-*co*-acrylonitrile) (SAN) were measured. It was found that the time–temperature superposition principle is applicable over the entire temperature range studied for the blends. The temperature dependency of the shift factors a_T can be expressed by the Williams–Landel–Ferry equation: $\log a_T = -8.86(T - T_s)/(101.6 + T - T_s)$. The compositional dependency of T_s represents the Gordon–Taylor equation. The zero-shear viscosities are found to increase concavely upward with an increase in weight fraction of SAN at constant temperature, but concavely downward at constant free volume fraction. It is concluded that the relaxation behavior of the PCL/SAN blends is similar to that of a blend consisting of homologous polymers. It is emphasized that the viscoelastic functions of the miscible blends should be compared in the iso-free volume state. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2037–2041, 2001

Key words: zero-shear viscosity; iso-free volume; miscible polymer blend; poly(ϵ-caprolactone); poly(styrene-*co*-acrylonitrile)

INTRODUCTION

Chiu and Smith[1,2] studied the miscibility of poly(ϵ-caprolactone) (PCL)/poly(styrene-*co*-acrylonitrile) (SAN) blends, which was characterized by the occurrence of a single, compositionally dependent glass transition intermediate between the transitions of the respective pure components. They found that SAN and PCL form miscible blends when the acrylonitrile (AN) content of SAN ranges from 8 to 28 wt %. Besides those for PCL/SAN blends, there have been many studies of miscibility of SAN with a homopolymer and a copolymer. It was previously reported that SAN is miscible with poly(methyl methacrylate) (PMMA),[3–5] poly[styrene-*co*-(maleic anhydride)] (SMA),[6–10] poly[(methyl methacrylate)-*co*-(N-phenylmaleimide)],[11] and poly[styrene-*co*-(N-phenylmaleimide)] (SMI),[10] when the AN content of SAN is within a specific range. It is believed that the miscibility of SAN with other polymers is mainly attributed to the thermodynamically unfavorable repulsion between St and AN segments in the random copolymer and, in general, there are no specific interactions between dissimilar chains.[12–14]

Han and Yang[15] studied the rheological behavior of miscible PCL/SAN blends. They found that logarithmic plots of the first normal stress difference N_1 versus shear stress σ_{12}, and logarithmic plots of the shear storage modulus G' versus the loss modulus G'' become virtually independent of temperature but vary with blend composition, and that the zero-shear viscosity of the blends $(\eta_0)_{\text{blend}}$ follows the relationship $1/\log (\eta_0)_{\text{blend}} = w_A/\log \eta_{0A} + w_B/\log \eta_{0B}$, where η_{0A} and η_{0B} are the zero-shear viscosities and w_A and w_B are the weight fractions of components A and B, respec-

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tively. They reported that this relationship is equivalent to asserting that the PCL/SAN blend system follows the additivity rule of the free volume.

One of the authors,[8,16,17] who investigated the rheological properties of miscible blends of SAN with (co)polymers in the molten state, found that log $(\eta_0)_{blend}$ versus blend composition curves for the SAN/SMI blends show negative deviation from linearity at constant temperature but show positive deviation at an iso-free volume fraction. On the other hand, it was found that log $(\eta_0)_{blend}$ versus blend composition curves for the SAN/PMMA blends deviate positively from linear additivity at both constant temperature and free volume fraction. He concluded that log $(\eta_0)_{blend}$ is a function not only of the free volume but also of the number of entanglement couplings.

In this study the dynamic viscoelastic properties of miscible PCL/SAN blends were measured, employing a strain-controlled rheometer with plate–plate geometries. To elucidate the viscoelastic properties without specific interactions between dissimilar chains, compositional dependencies of the shift factors and zero-shear viscosities were studied. The results are discussed in terms of the free volume concept and entanglement couplings.

EXPERIMENTAL

The samples used in this study were commercial poly(ϵ-caprolactone) (PCL; purchased from Sowa Science Co., Tokyo) and poly(styrene-*co*-acrylonitrile) (SAN; obtained from Techno Polymer Co., Mie). GPC measurements using tetrahydrofuran (THF) as solvent and calibrated with standard polystyrene gave the following molecular characteristics for PCL: $M_w = 1.7 \times 10^4$ g/mol and $M_w/M_n = 2.0$; and for SAN: $M_w = 9.4 \times 10^4$ g/mol and $M_w/M_n = 2.2$. The acrylonitrile (AN) content in the SAN was determined by elemental analysis and found to be 24.2 wt %.

For purification and to prepare blends of various compositional ratios, coprecipitation of SAN and PCL was conducted, using THF and *n*-hexane as solvent and precipitant, respectively. The blend composition ratios were PCL/SAN = 0/100, 20/80, 40/60, 60/40, 80/20, and 100/0 by weight. First, the PCL was completely dissolved in 100 mL of THF. After that the corresponding amounts of SAN were added, so that the total amount of polymers was 4 g in 100 mL THF. After addition of 50 mL of *n*-hexane, which served as a nonsolvent in this case, the solutions were stirred overnight. The solutions were then slowly added into another 700 mL of *n*-hexane to complete coprecipitation and to obtain fine powders. These were subsequently dried under vacuum at 50°C. After that, compression molding was carried out to produce the specimens that were tested in the rheometer. Thus the blends were heated for 5 min at 160°C, pressed for 3 min at 160°C and 100 kg/cm², and then pressed for 5 min at ambient temperature and 150 kg/cm².

The rheological measurements were carried out using a dynamic ARES-2KFRTN1 rheometer of Rheometric Scientific (Tokyo). The rheometer uses two amplification settings to provide the torque measurement to range from 0.2 to 2000 g cm. Then 25-mm-diameter parallel plates were used for dynamic measurements. Shear storage modulus G' and loss modulus G'' were measured as functions of angular frequency ω, at temperatures between 80 and 160°C for pure PCL, between 140 and 220°C for pure SAN, and between 100 and 160°C for the PCL/SAN blends. Depending on the viscoelastic properties of each sample, a suitable shear amplitude γ was used to ensure the linearity of dynamic viscoelasticity.

RESULTS AND DISCUSSION

The G' and G'' for the component (co)polymers and blends were measured as functions of ω. Measurements were taken at different temperatures to investigate the temperature dependency of the viscoelastic properties. The frequency-dependency curves of G' and G'' at various temperatures were superimposed onto the master curves at 160°C. The temperature dependency of the shift factors a_T became slightly steep with an increase in SAN content, when the reference temperature was 160°C for all samples. However, when the reference temperatures T_s were chosen to be 140, 92, 61, 25, and 0°C for PCL/SAN = 0/100, 20/80, 40/60, 60/40, and 80/20, respectively (for pure PCL we could not precisely determine the T_s from the temperature dependency of a_T), all the curves could be expressed by a single Williams–Landel–Ferry (WLF) equation,[18] shown in Figure 1,

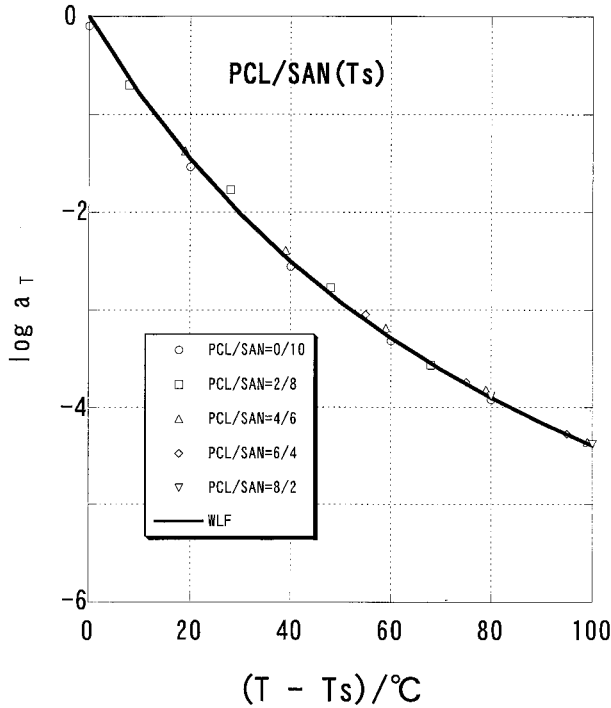$$\log a_T = -c_1(T - T_s)/(c_2 + T - T_s) \qquad (1)$$

Figure 1 Temperature dependency of the shift factors a_T for the PCL/SAN blends.

where T is the temperature, T_s is the reference temperature, $c_1 = 8.86$, and $c_2 = 101.6$. It is said that the WLF equation is applicable to temperatures that are approximately 100°C above the glass-transition temperature T_g. However, our previous studies show that the WLF equation is applicable to higher temperatures for SAN and miscible SAN blends.[8,16,17] 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 dependency of T_s for the PCL/SAN blends. It is said that the T_s expressed by eq. (1) is about 50°C higher than the T_g for many polymers.[18] Chiu and Smith[1] reported that the compositional dependency of the T_g for SAN/PCL blends represents the Gordon–Taylor equation[19]:

$$T_s^{\text{blend}} = T_s^{\text{PCL}} + K(T_s^{\text{SAN}} - T_s^{\text{blend}})w^{\text{SAN}}/w^{\text{PCL}} \quad (2)$$

where w^{SAN} and w^{PCL} are the weight fractions, T_s^{SAN} and T_s^{PCL} are the T_s of pure SAN and PCL, respectively, and T_s^{blend} is the blend T_s. For a miscible system, the plot of T_s^{blend} versus $(T_s^{\text{SAN}} - T_s^{\text{blend}})w^{\text{SAN}}/w^{\text{PCL}}$ will yield a straight line with a slope of the empirical constant K and an ordinate intercept of T_s^{PCL}. The data were fitted by a

least-squares regression technique, and the slope of the straight line was found to be about 0.6. The T_s of PCL obtained as the ordinate intercept was 250 K. The broken line in Figure 2 indicates the Gordon–Taylor equation in the case of $K = 0.6$ and $T_s^{\text{PCL}} = 250$ K. Chiu and Smith's data are essentially equivalent to our results. PCL (low T_g component) is considered as a diluent for SAN (high T_g component).

Parts (a) and (b) of Figure 3 show the master curves of G' and G'' for the PCL/SAN blends as a function of ω. At low frequencies, G' is proportional to ω^2 and G'' is proportional to ω for each sample. This is a Newtonian flow region in which the dynamic viscosity $\eta' = G''/\omega$ is independent of frequency. Therefore, the zero-shear viscosity η_0 can be calculated from these data.

Figure 4(a) shows the compositional dependency of the zero-shear viscosity η_0 at constant temperature. The η_0 values increase concavely upward with an increase in weight fraction of SAN, as found by Han and Yang.[15] However, compositional dependencies of η_0 were found to vary with temperature. This fact implies that the η_0 behavior is affected by a free volume within the blends. Figure 4(b) shows the compositional de-
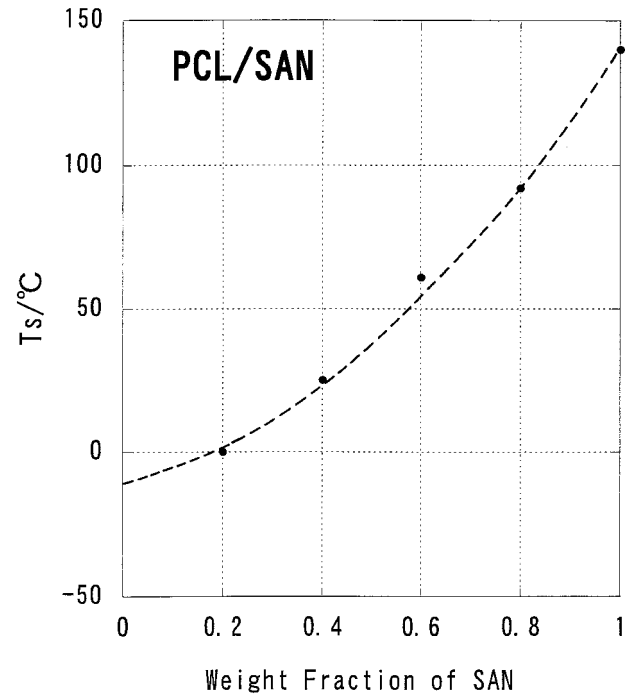

Figure 2 Compositional dependency of the reference temperature T_s for the PCL/SAN blends. The broken line indicates the Gordon–Taylor equation in the case of $K = 0.6$ and $T_s^{\text{PCL}} = 250$ K.
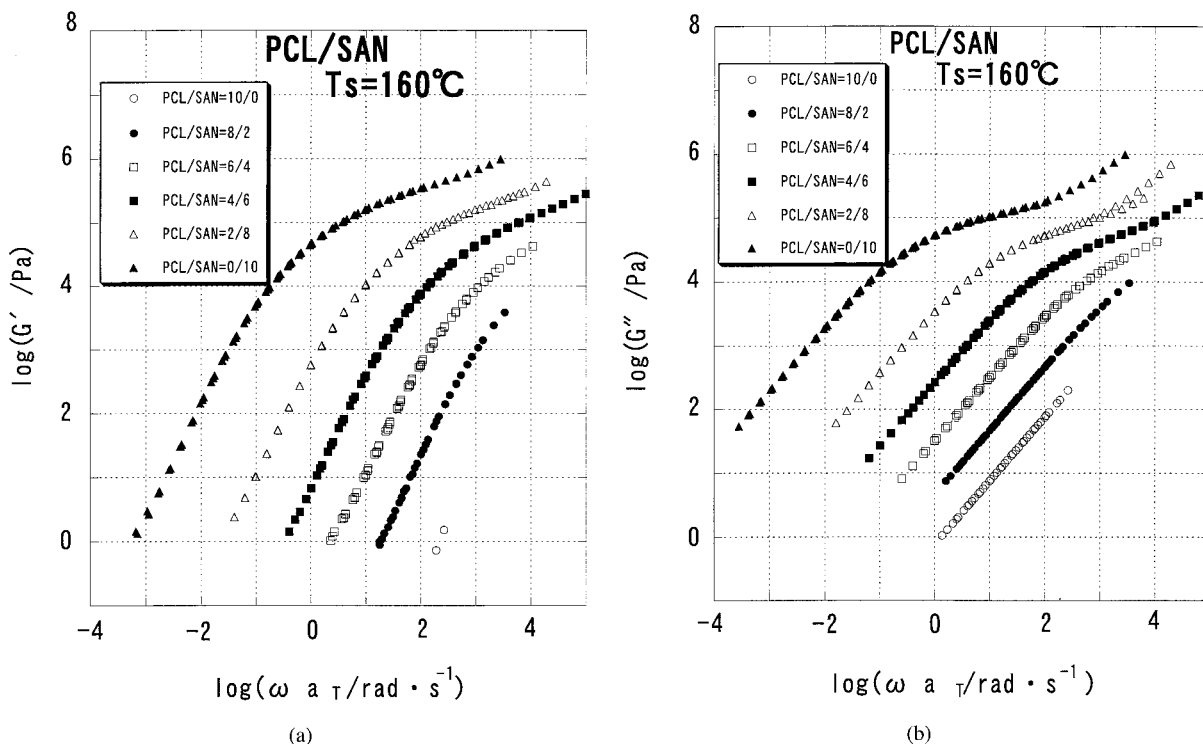
Figure 3 Master curves of the storage modulus G' (a) and loss modulus G'' (b) as a function of angular frequency ω for PCL/SAN blends of different compositions (T_s = 160°C).

pendency of η_0 at a constant free volume fraction of $f = 0.049$ ($T = T_s$), where the η_0 of pure PCL was estimated from $T_s = 250$ K. η_0 increases concavely downward with an increase in weight fraction of SAN.

Previously, we proposed that the rheological behavior of miscible blends should be compared at an iso-free volume condition.[16,17] Assuming the additivity of the number of entanglement couplings (n_w^j) in the blends instead of the additivity of the molecular weight,

$$n_w^{\text{blend}} = w^{\text{PCL}}n_w^{\text{PCL}} + w^{SAN}n_w^{SAN} \qquad (3)$$

we 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 preceding proposal to PCL/SAN blends. Using eq. (3) and $\eta_0 = \text{const.}(n_w^{\text{blend}})^{3.8}$, where $n_w^{\text{PCL}} = 3.3$ and $n_w^{SAN} = 7.1$, the η_0 values of the PCL/SAN were calculated according to the method of previous studies.[16,17] The broken line in Figure 4(b) indicates the calculated values. It is found that the calculated values are in good agreement with experimental values. When compared at an iso-

free volume condition, the compositional dependency curve is the same as that of a blend consisting of two homologous polymers with different molecular weights. Then, it is concluded that the entanglement couplings of the PCL/SAN blends are identical to those in the component polymers.

CONCLUSIONS

It was found that the zero-shear viscosity change of miscible PCL/SAN blends at constant temperature consists of two terms: the free volume change and the change of number of entanglement couplings. The free volume change can be estimated from the temperature dependency of the shift factors a_T. Because the time–temperature superposition principle is applicable over the entire investigated temperature range for the PCL/SAN blends, the temperature dependency of a_T could be expressed by the WLF equation: $\log a_T = -8.86(T - T_s)/(101.6 + T - T_s)$. The change of number of entanglement couplings can be estimated from the compositional dependency of the zero-shear viscosity at an iso-free volume condi-
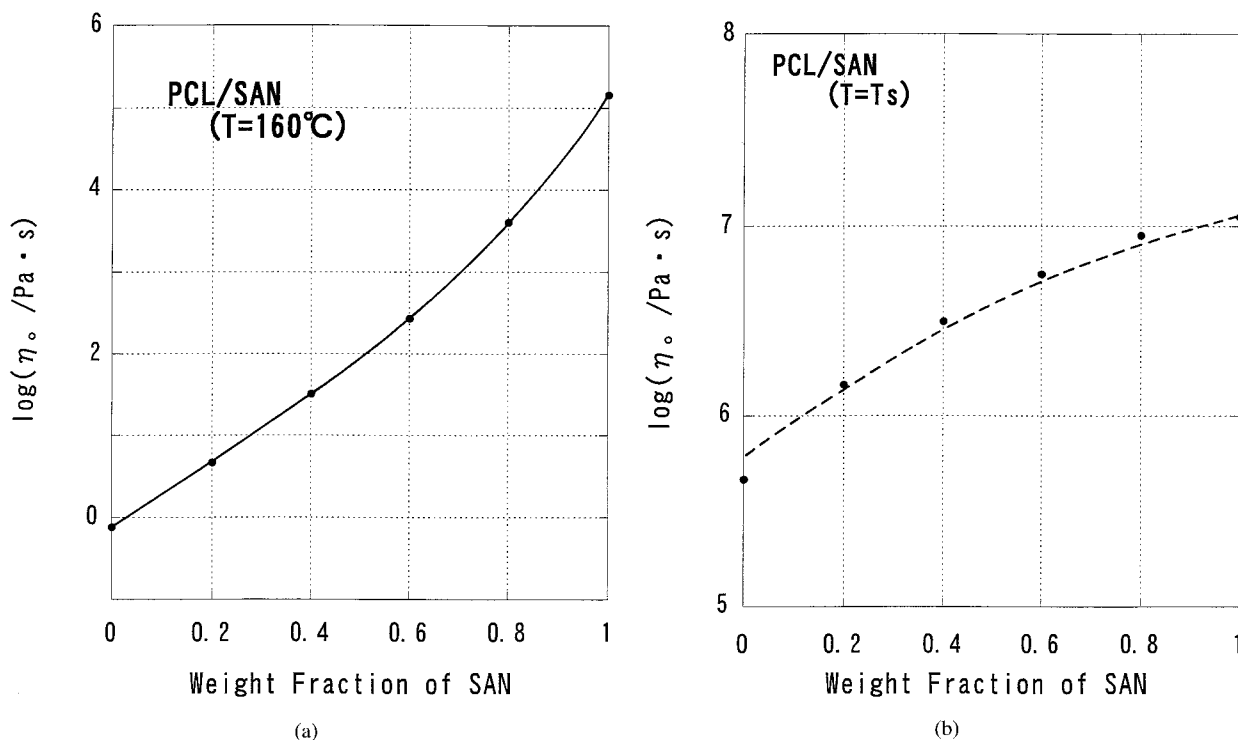
Figure 4 Compositional dependency of the zero-shear viscosity η_0 for PCL/SAN blends at constant temperature of 160°C (a) and constant free volume fraction of 0.049 (b). The broken line indicates the calculated values. The calculation method is shown in the text.

tion. It is concluded that the relaxation behavior of the PCL/SAN blends is similar to that of a blend consisting of homologous polymers. It is emphasized that the viscoelastic functions of miscible blends should be compared at an iso-free volume condition to discuss the change in number of entanglement couplings.

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