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Rheological properties of poly(ε-caprolactone) and poly(styrene-co-acrylonitrile) blends

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SUMMARY

Rheological properties of poly(ε-caprolactone) (PCL) and Poly(styrene-co-acrylonitrile) (SAN) blends were examined as a function of the acrylonitrile (AN) content in SAN, to systematically understand the correlation between the interaction parameter and the rheological properties of miscible polymer blends. When the plateau modulus (G_N^0) and zero shear viscosity (η_0) of the PCL/SAN blends are plotted against the AN content in SAN, a minimum is observed. Qualitatively, the results obtained parallel the variation of the interchain interaction with the AN content. The negative deviation of G_N^0 and η_0 from linearity seems to be attributed to the increase in the entanglement molecular weight between dissimilar chains which results from the chain extension caused by interchain interaction.

INTRODUCTION

Polymer blends, as an excellent way of formulating new materials with tailored properties, have been of considerable interest in recent years. This technique is a simple method used to obtain properties not readily achieved in a single polymer. Besides practical interest, during the past two decades, there has not only been reports on many compatible polymer blends having dissimilar chemical structures, but also efforts to increase the miscibility of polymer blends. Together with these efforts, many investigations have reported the rheological behavior of compatible blends, which is especially focused on the deviation of the logarithmic zero shear viscosity ($log\eta_0$) with blend composition.

Several mixing rules for the rheological properties of polymer blends have been reported, namely a logarithmic additive rule(1), a mixing rule based on the free volume theory(2), and a mixing rule based on the entanglement probability(3). However, these rules do not take into account the interaction parameter which is very important for miscible polymer blends. Very recently, Han and Kim(4) reported on the rheological properties of PMMA/SAN and PVDF/PMMA blends using the concept of Doi and Edwards' tube model. They regarded the interaction parameter (χ) between two polymers as an external potential and derived an expression for the relaxation modulus of the blends $G_b(t)$ using the 3.4-power blending or linear blending law, and then calculated zero shear viscosity of blends η_{0b} which contains the interaction parameter.

In this study, the rheological properties of polymer blends containing a copolymer have been examined as a function of copolymer composition in order to systematically interpret the effect of the interchain interaction on rheological properties of polymer blends. The comonomer content in a copolymer provides a useful way in systematically varing the strength of a polymer-polymer pair interaction . The PCL/SAN blends are chosen for this purpose, since it is well known that SAN copolymers are miscible with PCL over a certain range in AN content(5).

EXPERIMENTAL

Materials Table I lists the properties of polymers used in this study. All of the SAN copolymers in Table I are miscible with PCL since it is known that SAN copolymers containing AN contents of 8-28 wt% are completely miscible with PCL(5). SAN's have similar molecular weights, which excludes the effect of molecular weight on zero shear viscosity.

Preparation of blend samples Blend samples for the rheological measurements were prepared according to the following procedure: [1] Mixtures of PCL/SANs (1/1, w/w) were dissolved in tetrahydrofuran followed by precipitation in a large excess of n-hexane; [2] The precipitated mixture was dried slowly at room temperature for 1 day in a hood and then under vacuum at 60°C for two days; [3] The dried PCL/SAN mixtures in the form of flakes were compression molded into a sheet of about 1mm in thickness at 150°C using a hot press.

Table I. Polymer characterization used in this study

polymer	copolymer composition, wt %	M_w	source
PCL	-	74,000	Aldrich Co.
SAN11.5	11.5	198,000	Asahi Co.
SAN14.7	14.7	181,000	Asahi Co.
SAN19.5	19.5	198,000	Asahi Co.
SAN25	25.0	160,000	Aldrich Co.

Rheological measurement A Rheometrics mechanical spectrometer (RMS 800E) with a parallel plate mode was used for the measurement of the dynamic storage modulus (G'), the dynamic loss modulus (G''), and the shear viscosity (η) as a function of angular frequency (ω) in dynamic mode. The rheological properties of the blends were measured at various temperature (95 - 155°C) from the plateau to melt region under a nitrogen atmosphere. Strain was maintained at 10% for all of the samples. The plateau modulus (G_N^0) was determined as the storage modulus at the frequency where $\tan \delta$ shows a minimum.

RESULTS AND DISCUSSION

The miscibility of PCL/SANs used in this study has been investigated by various research groups. Chiu and Smith(5) have reported the miscibility of PCL/SAN blends over the entire range of blend compositions using a differential scanning calorimeter (DSC) and a dynamic mechanical analyzer. They have found that PCL is miscible with SANs containing AN contents which are greater than 8 wt% but less than 28 wt%. Fernandes et al.(6) estimated the segmental interaction parameters B_{ij}'s in the PCL/SAN blends from the melting point depression analysis. However, their data is not accurate because they used the apparent melting temperatures. Very recently, Jo and Kim(7) evaluated segmental interaction parameters of the blend system by using the equilibrium melting point depression. When the segmental interaction parameters are substituted into the binary interaction model proposed by Paul and Barlow(8), the overall interaction parameters for PCL/SAN are calculated as a function of AN contents in SAN as shown in Fig. 1.

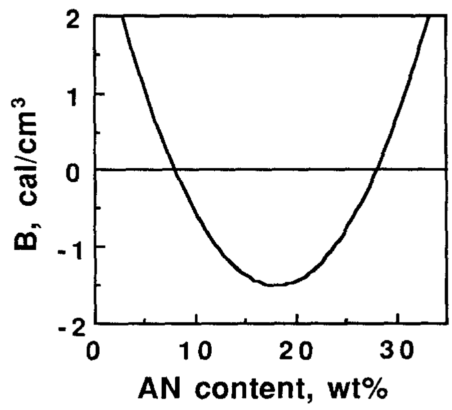

Figure 1. Variation of the net interaction energy density (B) with AN content in SAN copolymers for PCL/SAN blends. Segmental interaction parameters Bij's to evaluate B were taken from the literature(7).

The storage modulus and loss modulus are plotted against frequency for the PCL/SAN blends as shown in Fig. 2. The moduli were measured at 95℃, which corresponds to the plateau region. As mentioned above, the plateau modulus(G_{Nb}^{0}) was determined as G'' at the frequency where *tan* δ shows a minimum. Figure 3 shows the dependence of G_{Nb}^{0} and its inverse ($1/G_{Nb}^{0}$), which is related to the entanglement molecular weight (M_e) by the relation $G_N^0 = \rho RT/M_e$, on the AN contents in SAN copolymers. G_{Nb}^{0} and $1/G_{Nb}^{0}$ have a minimum and maximum point, respectively. When Fig. 1 is compared with Fig. 3, G_{Nb}^{0} agrees qualitatively with the deviation of the interaction parameters, while $1/G_{Nb}^{0}$ is inversely proportional to the interaction parameter, which indicates that the entanglement probability between dissimilar chains becomes smaller as the interchain interaction becomes stronger(i.e. more negative B). This phenomenon can be explained by following explanation.

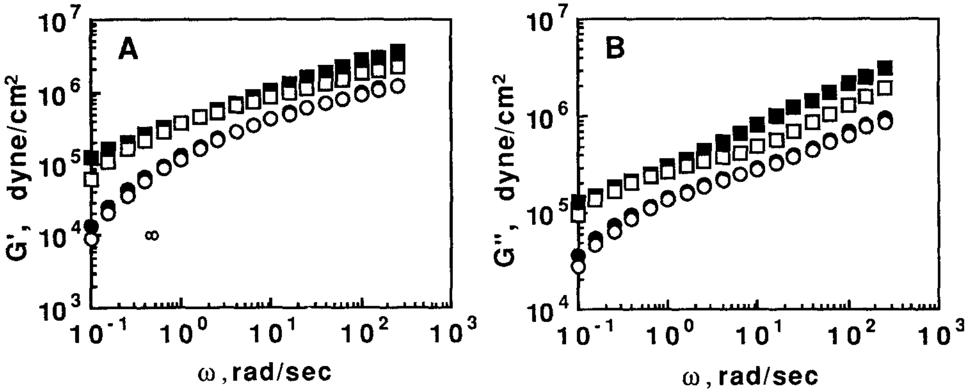

Figure 2. Storage modulus (G') (A) and loss modulus (G'') (B) versus frequency at 95°C for PCL/SAN blends: ■, PCL/SAN11.5; ●, PCL/SAN14.7; ○, PCL/SAN19.5; □, PCL/SAN25.

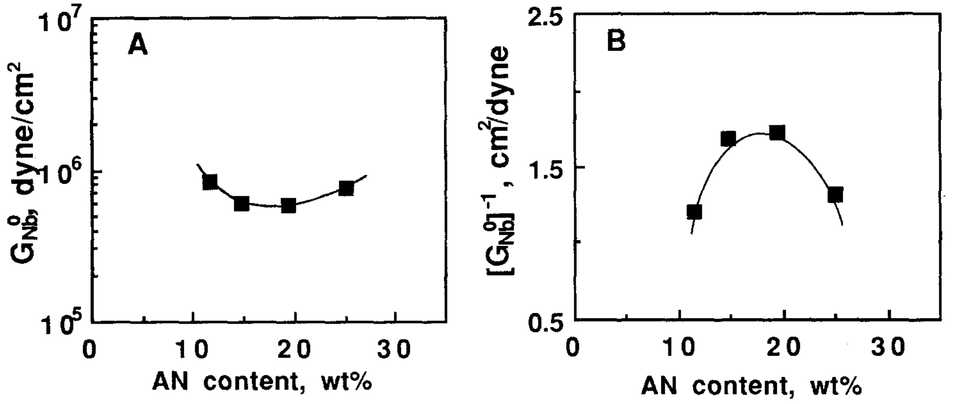

Figure 3. The variation of plateau modulus (G_{Nb}^{0}) (A) and the reciprocal plateau modulus ($1/G_{Nb}^{0}$) (B) with AN content in SAN copolymers for PCL/SAN blends. The plateau modulus was determined as a loss modulus where *tan* δ shows a minimum.

Recently, Wu(3, 9, 10) has explained the rheological properties of miscible blends in terms of entanglement, friction coefficient, free volume, and molecular weight. He considered the pair interactions, i.e., 1-1, 2-2, and 1-2 interaction points. Assuming that the entanglement molecular weight of the two dissimilar chains in the blend is the same as that of a hypothetical pure component of density $(\rho_1\rho_2)^{1/2}$, Wu obtained eq 1 with the aid of the relation $G_{Nb}^{0} =$

$\rho RT/M_e$.

$$G_{Nb}^0 = \phi_1 G_{N1}^0 + \phi_2 G_{N2}^0 + \phi_1\phi_2(\lambda_e - 1)(G_{N1}^0 + G_{N2}^0) \quad (1)$$

where $G_{Nb}{}^0$ is the plateau modulus of the blend, $G_{Ni}{}^0$ is the plateau modulus of the component polymer, ϕ_i is the volume fraction, and λ_e is given by eq 2.

$$\lambda_e = \frac{\left[(\rho_1\rho_2)^{1/2}/M_{e12}\right]}{\left[(\rho_1/M_{e1} + \rho_2/M_{e2})/2\right]} \quad (2)$$

Note that λ_e can also be given by $\lambda_e = p(12)/p(12, \theta)$, in which $p(12)$ and $p(12, \theta)$ are the entanglement probabilities per 1-2 contact in a real blend, and in a θ-blend($B = 0$), respectively. Wu explained that $G_{Nb}{}^0$ of miscible polymer blends should show negative deviations from linearity, indicating that λ_e is less than unity. He concluded that the specific interchain interaction tends to locally align the chain segments for association, and thus stiffens the chains and reduces their convolution, which results in the reduced entanglement between chains.

The melt viscosity is plotted against frequency at 140 and 155°C in Fig. 4. For all samples, it is typically observed that the viscosity has a Newtonian region at low frequency and a yield region at high frequency. When zero shear viscosities are plotted against the AN content in SAN (Fig. 5), it is also observed that the zero shear viscosities show a strongly negative deviation and a minimum. This phenomenon qualitatively corresponds to the deviation of $G_{Nb}{}^0$ and the interaction parameters. As discussed above, specific interaction tends to locally align the chain segments, resulting in reduced entanglement between dissimilar chains, and thus viscosity increases with interchain interaction.

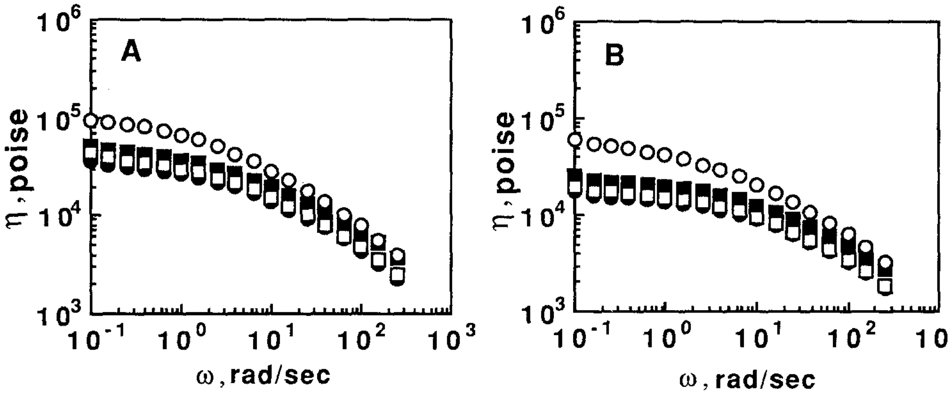

Figure 4. Melt viscosity versus frequency at 140°C(A) and 155°C(B) for PCL/SAN blends: ■, PCL/SAN11.5; ●, PCL/SAN 14.7; ○, PCL/SAN 19.5; □, PCL/SAN 25.

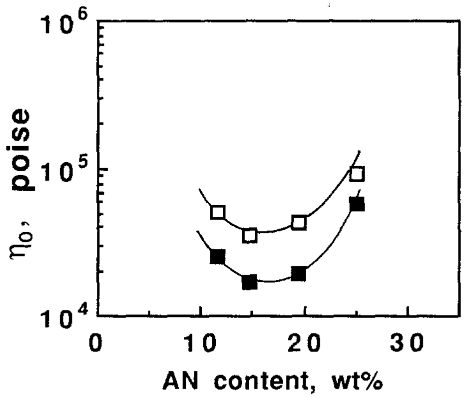

Figure 5. The variation of zero shear viscosity with AN content in SAN copolymers at 140°C(□) and 155°C (■) for PCL/SAN blends.

CONCLUSIONS

The use of SAN series having similar molecular weights excludes the molecular weight effect on the rheological properties of PCL/SAN blends and provides a useful way of systematically varying the strength of the interaction of the polymer-polymer pair. $1/G_{Nb}{}^0$

and η_0 have a maximum and a minimum at a certain AN composition, respectively. In a qualitative sense, these results parallel the variation of the interchain interaction with AN content. Therefore, it is concluded that the specific interaction tends to locally align the chain segments for association, resulting in the reduced entanglement between dissimilar chains, and thus the plateau modulus and zero shear viscosity increases and decreases respectively as the interchain interaction becomes stronger(more negative B).

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