Plateau Modulus of Homogeneous Polystyrene/Poly(vinyl methyl ether) Blends

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Viscoelastic properties of miscible binary polymer blends depend on various factors such as the molecular weights and compositions of the components and the interactions between them.

In a previous work,¹ we studied the zero-shear viscosity, η^0 , and steady state compliance, J_e , of homogeneous polystyrene/poly(vinyl methyl ether) (PS/PVME) blends with different molecular weights of PS, M_{PS} , and a constant molecular weight of PVME, M_{PVME} , maintaining the condition $M_{PS} \gg M_{PVME}$. M_{PVME} was 3.7×10^4 which is slightly larger than the molecular weight between entanglements, $M_e (=1.24 \times 10^4)$.² Entanglements between PVME chains with such molecular weight are at most 1 or 2 per chain even in melts.

We reported that the PS volume fraction, ϕ_{PS} , dependence of zero-shear specific viscosity, η_{sp}^0 , at $\phi_{PS} < 0.3$ can be classified into dilute and semidilute regimes by critical ϕ_{PS}^* values, ϕ_{PS}^* and η_{sp}^0 can be explained by the scaling theory³ in the semidilute regime where PS chains are entangled with each other, in the same way as in polymer solutions.⁴ Here, $\eta_{sp}^0 = (\eta^0 - \phi_{PVME}\eta_{PVME}^0)/\eta_{PVME}^0$, η_{PVME}^0 is the zero-shear viscosity of PVME and $\phi_{PVME} = 1 - \phi_{PS}$. In the same ϕ_{PS} region, on the other hand, J_e exhibited the non-entangled regime behavior as those observed in corresponding polymer solutions, because the larger amounts of entanglements are needed to give the entangled regime behavior for J_e .^{5–7}

In this work, we study the plateau modulus, G_N , of PS/PVME blends to clarify the elastic property of the miscible blends in semidilute regime instead of J_e . Here, we use a PVME sample with molecular weight lower than the previous sample, as well as the previous one to assure that the entanglements are composed of PS chains only.

EXPERIMENTAL

PVME samples used in this work were the previous one (fractionated one; $M_w = 3.7 \times 10^4$, $M_w/M_n = 1.32$) and a new one which was prepared by cationic polymerization in our laboratory following a literature,⁸ but using different terminator, $LiBH_4$.⁹ The number-average molecular weight, M_n , and the molecular weight distribution index, M_w/M_n , were determined to be 2.2×10^4 and 1.18 by 1H NMR (unity-INOVA, Varian) and GPC (with Tosoh GMHXL mixed column $\times 2$), respectively. Hereafter, we call the previous one as PVME1 and the

new one as PVME2. M_n of PVME2 is about twice higher than M_e for PVME in melts,² so that the entanglements of PVME chains are safely negligible in the blends with $\phi_{PS} < 0.3$. The PS samples were the same Tosoh standard polystyrenes with narrow molecular weight distributions, used in the previous work¹; F-20 ($M_w = 1.9 \times 10^5$), F-40 ($M_w = 3.6 \times 10^5$), F-80 ($M_w = 7.1 \times 10^5$), and F-126 ($M_w = 1.26 \times 10^6$). The preparation method of blend samples is the same as in the previous work.¹

Rheological measurements were performed with a Mechanical Spectrometer RMS800 of Rheometrics Inc. using a parallel plate geometry with 2.5 cm diameter. Dynamic frequency sweep measurements were performed at several different temperatures (323–373 K) and all the data were shifted to the reference temperature $T_r = 353.6$ K in accordance with the WLF equation for PVME.² This procedure was justified in the previous work,¹ that is, the temperature dependence of shift factors, a_T , of the blends agree with that of PVME. Dry nitrogen gas was introduced in the temperature control system of the RMS800 to prevent the oxidation of PVME and also the absorption of moisture.

RESULTS AND DISCUSSION

Examples of master curves of storage (G') and loss (G'') moduli of a PS/PVME2 blend at 353.6 K are shown in Figure 1. Some master curves of PS/PVME1 blends

Figure 1. Example of the master curves of G' , G'' , and $\tan \delta$ at 353.6 K as a reference temperature. The sample is F-40/PVME2 blend with $\phi_{PS} = 0.244$.

Figure 2. Double logarithmic plots of (a) η_0^0 vs. ϕ_{PS}/ϕ_{PS}^* for the blends and (b) J_{eR} vs. $\phi_{PS}M_{PS}$. Different symbols denote difference of PS samples. The open and filled symbols denote the data of the blends with PVME1 and PVME2, respectively. Solid line in (a) denote the slope of scaling prediction, while solid and dashed lines in (b) denote the data of PS solutions in non-entangled and entangled regions, respectively.¹

are already reported in the previous paper.¹ Hereafter, all the rheological data will be discussed at this temperature. η^0 and J_e obtained in this work are consistent with the previous data¹ as shown in Figures 2a and b in the form of η_{sp}^0 vs. ϕ_{PS}/ϕ_{PS}^* and reduced steady state compliance $J_{eR} [(J_e\phi_{PS}RT/M_{PS})\{\eta^0/(\eta^0 - \eta_{PVME}^0)\}^2]$ vs. $\phi_{PS}M_{PS}$, respectively.

In the master curves of the blends with relatively low ϕ_{PS} 's, the G' values are lower than the G'' values over all the ω range. On the other hand, in the master curves of the blends with relatively high ϕ_{PS} 's ($M_{PS}\phi_{PS} > 26000$), the G' values become higher than the G'' values at the intermediate ω range, so that we can evaluate the plateau moduli, G_N . Here, we determined G_N as the G' value at which $\tan \delta [=G''/G']$ value has a minimum as illustrated in Figure 1.

Figure 3 shows double logarithmic plots of G_N against ϕ_{PS} . The dashed line in Figure 3 represents the G_N data for PS solutions in *n*-benzyl buthyl phthalate¹⁰ (the reported concentration dependence is $C^{2.2}$ to $C^{2.3}$) plotted against polymer concentration instead of ϕ_{PS} . A similar concentration dependence ($C^{2.4}$) was also reported for PS solutions in Aroclor 1248.¹¹ The G_N magnitudes of the blends and the solution are quite similar, confirming the previous conclusion¹ that the entanglements are composed of PS chains only.

The experimental ϕ_{PS} dependence of G_N determined

Figure 3. ϕ_{PS} dependence of G_N for the blends at $\phi_{PS} > \phi_{PS}^*$. The data of PS in *n*-benzyl buthyl phthalate¹⁰ are represented by the dashed line with the slope of 2.2. Symbols are the same as in Figure 2.

by least squares method is given as

$$G_N \propto \phi_{PS}^{2.2 \pm 0.1} \quad (4)$$

If the scaling theory³ is applicable to G_N , G_N is given by $G_N \propto \phi_{PS}^{3\nu/(3\nu-1)}$. Introducing $\nu = 0.53$ used for the viscosity data as shown in Figure 2a,¹ we have $G_N \propto \phi_{PS}^{2.7}$ for the PS/PVME blends, while we have $G_N \propto \phi_{PS}^2$ for the uniform network model. The experimental exponent is slightly larger than that of the uniform network model, but still much smaller than the value predicted by the scaling theory. As shown in Figure 3, the exponents of the blends and PS solution are practically the same. The exponents (2.2 to 2.3) for PS solution is nearly equal to the scaling prediction with $\nu = 0.6$, but the data in semidilute region was smoothly connected with the data in highly concentrated region and melts by a straight line, just like the data of J_e .⁷ It was pointed out that the scaling theory need not to be brought in to understand concentration dependence of J_e .⁷ Likewise, the data for polymer blends can be smoothly extrapolated to melt data of PS, having an intermediate exponent of the scaling and uniform network model. Thus, we conclude that the ϕ_{PS} dependence of the plateau modulus, *i.e.*, the elastic property of homogeneous polymer blends is practically understood by the uniform network model similarly to polymer solutions.⁵⁻⁷

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