Compatibility in Blends of Poly(2,6-Dimethyl Phenylene Ether)/Styrene-Acrylonitrile Copolymer

INTRODUCTION

It is well known that blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPE) and polystyrene (PS) are miscible and phase separation is not observed. Molecular compatibility of PPE with PS has been demonstrated over the whole composition range.[1-3] The interaction parameter $\chi_{PPE/PS}$ between PPE and PS was estimated to be about 0.1.[4] Blends of PPE with copolymers containing styrene are of interest recently and poly(styrene-co-acrylonitrile) (SAN) is one of them. Blends of PPE and SAN were investigated by Kressler and Kammer[5] and found to be miscible for SAN containing acrilonitrile less than 10.5%. Miscible blends with low content of acrylonitrile exhibited single glass temperatures (T_g). When the acrylonitrile content increased, two glass transition temperatures were observed.

In this work, we investigated the miscibility of PPE with SAN whose acrilonitrile content was 25%. The SAN with this composition was chosen because of its commercial interest. The glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) and dynamic mechanical measurements were performed. The miscibility window can be found directly from T_g behavior of blends.

For partially miscible systems like PMMA/PC, Kim and Burns[6] obtained compositions of two phases in equilibrium from T_gs of those phases. They then calculated an interaction parameter based on the Flory–Huggins theory. The interaction parameter for PPE/SAN system was calculated utilizing the same technique.

EXPERIMENTAL

Blends of PPE (M_n = 17,000, M_w = 36,200) and SAN [M_n = 15,000, M_w = 312,000] were prepared by a Buss Kneader (Model MDK/E46, Buss AG, Basel, Switzerland) with average residence time of 30 s. Barrel and die temperature was set to 290°C. The blends passed through a cooling water bath and pelletized. Differential scanning

calorimeter (DSC) measurements were carried out using a Perkin–Elmer 7 Series thermal analyzer under a nitrogen atmosphere with heating rate of 20°C min^{-1}. The heat flow difference between 10 mg sample in a sealed pan and a similar empty pan was recorded. The sealed aluminum pan is capable of withstanding 30 psia. The glass transition temperatures by DSC in this report were determined at the half height temperature of the heat capacity jump. The error of T_g determination using DSC measurements is ±0.1°C; thus the experimental precision is high enough in this study. Dynamic mechanical measurements were performed with a rheometric mechanical spectrometer (RMS, model 605, Rheometrics, Inc.) to confirm T_g behavior of DSC. The RMS specimens were subjected to an imposed oscillatory frequency of 2 Hz. Plots of tan δ against temperature were utilized to measure T_gs.

RESULTS AND DISCUSSION

Measurements of the glass transition temperatures were employed to study the miscibility of PPE/SAN systems as the difference in the T_gs of PPE and SAN is large enough. We designated T_g (PPE) for PPE-rich phases and T_g (SAN) for SAN-rich phases. PPE and SAN are found to be partially miscible. Figure 1 shows thermograms for pure PPE and a PPE/SAN blend. In this figure, PPO90/SAN10 means that overall concentration of PPE (or PPO) is 90%. As shown in Figure 1, T_g (PPE) decreases from 217.8°C for pure PPE to 215°C by adding 10% SAN. T_gs for blends for higher contents of SAN were obtained and are tabulated on Table I. It is shown that T_g (PPE) stays relatively constant with an increase in SAN beyond 10% SAN. Thus, the miscible region for the PPE-rich phase is between 0% SAN and 0%–10% SAN. A more accurate boundary point between miscible region and immiscible region may be found with more data pointing between 0 and 10 were it not for the difficulties involved in processing blends with a high content of PPE.

Similar T_g behavior occurs in the SAN-rich phase. Figure 2 and Table I show an increase in T_g (SAN) with addition of PPE up to about 6% PPE, after which point T_g stays relatively constant. Thus, the miscible region in the SAN-rich phase is between 94% SAN and 100% SAN. In Figure 3, T_g shift behavior of the blend was confirmed via RMS measurements. T_g (SAN) increased with an addition of 10% PPE. In Figure 4, T_g of Table I is plotted against blend overall composition. The graphical presen-
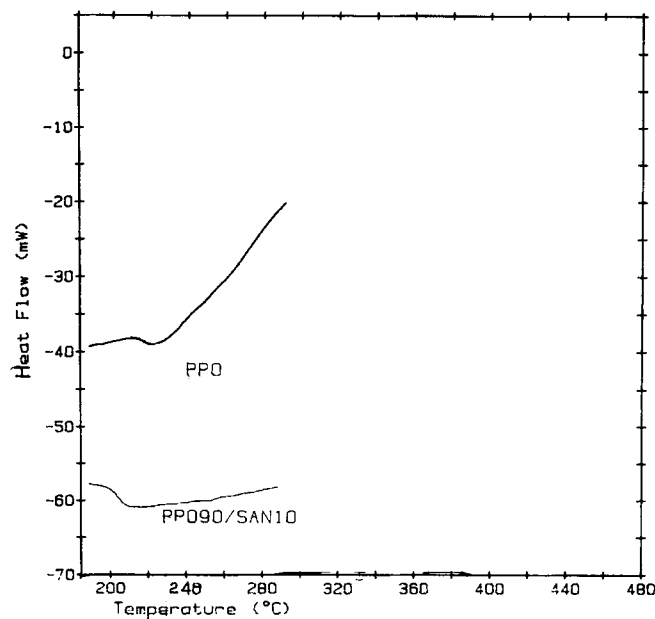
Figure 1   DSC thermogram of PPE and PPE 90%/SAN 10% blend.

tation clearly shows the T_g behavior described above. Lines approximating data points are hand drawn and an arrow for the SAN-rich phase indicates the point where the T_g stops increasing. This point is the boundary between the miscible and immiscible regions.

In the immiscible region, two T_gs for two phases do not vary as a function of blend overall concentration as in the miscible region. From the miscibility window described above, the compositions of two phases at equilibrium may be said to be 0–10% SAN in the PPE-rich phase

Table I T_g, **Composition of Immisible Phases in Equilibrium Calculated Using Eq. (2), and Interaction Parameter of PPE(1)/SAN(2) Blends**

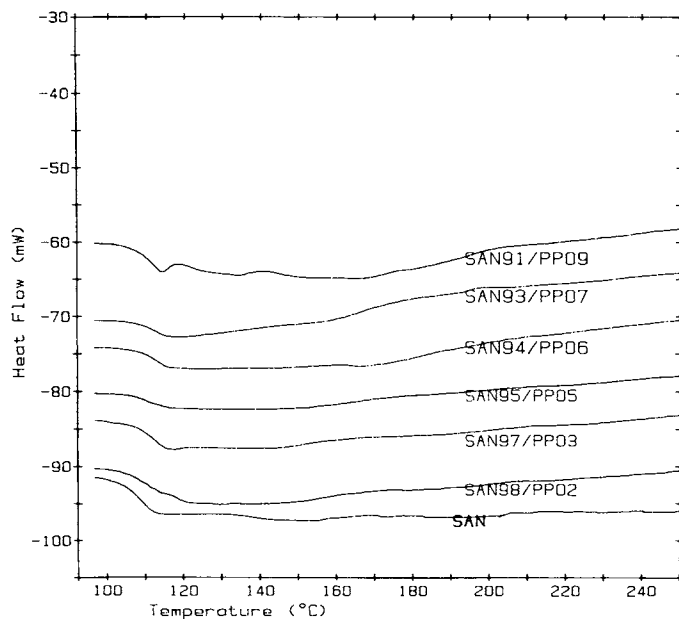| Blend (Wt. SAN)	T_g (PPE)	T_g (SAN)	ω_1'	ϕ_1'	ω_1''	ϕ_1''	Interaction Parameter [eq. (9)]	Interaction Parameter [eq. (10)]
0.00	217.80							
0.10	215.00	113.50	0.9745	0.9774	0.0501	0.0563	0.0163	0.0095
0.20	215.20	113.70	0.9763	0.9790	0.0519	0.0584	0.0161	0.0095
0.30	216.00	114.00	0.9836	0.9855	0.0546	0.0614	0.0158	0.0098
0.40	215.10	112.90	0.9754	0.9782	0.0446	0.0502	0.0169	0.0096
0.50	214.70	113.20	0.9718	0.9750	0.0474	0.0533	0.0166	0.0095
0.60	214.20	112.60	0.9672	0.9709	0.0419	0.0472	0.0173	0.0094
0.70	215.00	112.50	0.9745	0.9774	0.0410	0.0461	0.0174	0.0096
0.80		112.00						
0.90		112.10						
0.91		111.00						
0.93		112.00						
0.94		112.00						
0.95		111.00						
0.97		110.50						
0.98		110.00						
0.99		110.00						
1.00		108.00						

Figure 2 DSC thermogram of SAN and PPE/SAN blends with different compositions.
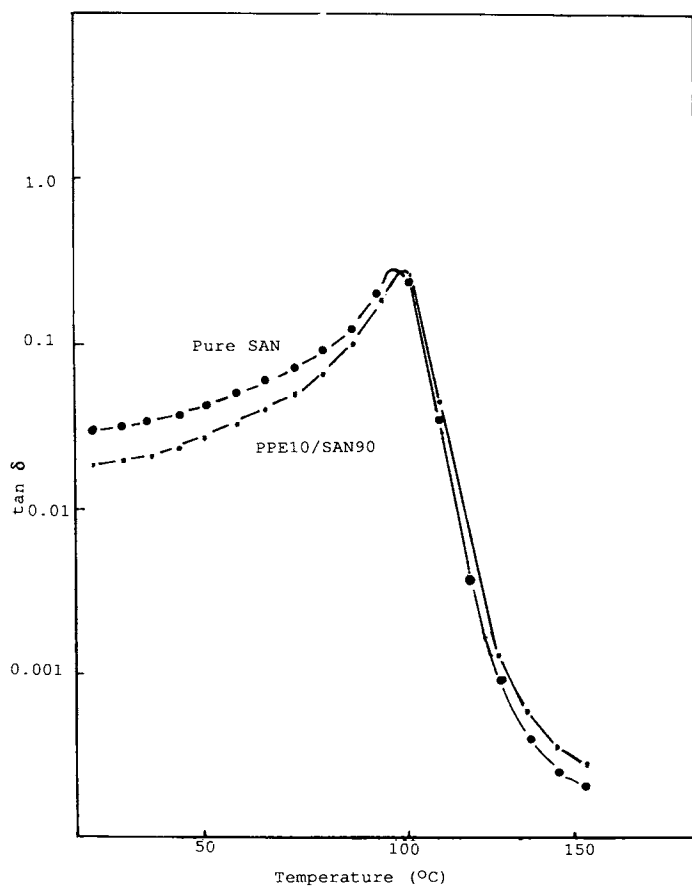

Figure 3 Dynamic mechanical results tan δ obtained by tortion rectangular.
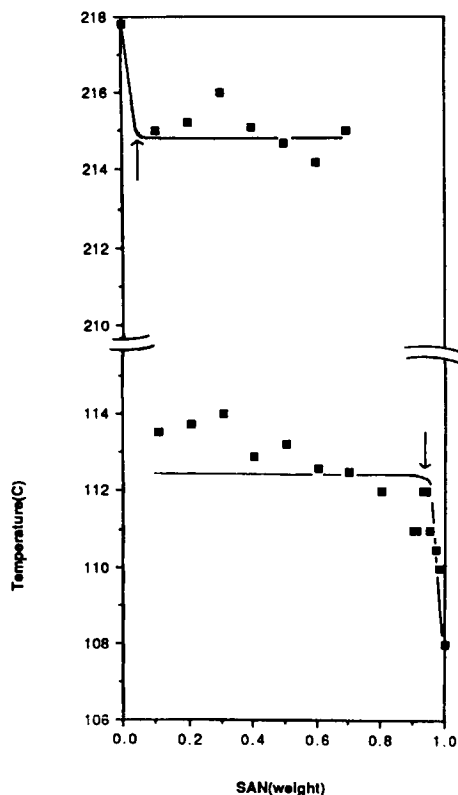
Figure 4 Effect of blend composition on T_g (PPE) and T_g (SAN) for PPE/SAN blends.

and about 94% SAN in the SAN-rich phase. But utilizing the techniques used by Kim and Burns,[5] the compositions of two phases at equilibrium can be deduced. For the immiscible region, the weight fractions of PPE can be determined in the PPE-rich phase and the SAN-rich phase by the following empirical equation, often used to describe the dependence of T_g on composition of blends, copolymers, and plasticized systems:

$$T_g = \omega_1 T_{g1} + \omega_2 T_{g2}, \tag{1}$$

where T_g is the observed T_g of the blend of the miscible system or the miscible region of a partially miscible system, ω_1 is the weight fraction of PPE having T_{g1}, and ω_2 is the weight fraction of SAN having T_g. Equation (1) may be rearranged to:

$$\omega_1' = \frac{T_{g1,b} - T_{g2}}{T_{g1} - T_{g2}}, \tag{2}$$

where ω_1' is the weight fraction of PPE in the PPE-rich phase, $T_{g1,b}$ is the observed T_g of PPE-rich phase in the blends, and T_{g1} and T_{g2} are the T_gs of PPE and SAN. In this manner, weight fractions of PPE in the PPE-rich phase (ω_1') and SAN-rich phase (ω_1'') were calculated as shown in Table 1. In the table, a prime denotes the PPE-rich phase and a double prime denotes the SAN-rich phase,

ω_1' and ω_1'' are weight fractions, and ϕ_1' and ϕ_1'' are volume fractions.

The alternative to eq. (1) is the Fox equation:

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}}, \tag{3}$$

which may be rearranged to

$$\omega_1' = \frac{T_{g1}(T_{g1,b} - T_{g2})}{T_{g1,b}(T_{g1} - T_{g2})}. \tag{4}$$

Equation (4) was used to obtain equilibrium compositions as shown in Table II. As shown in Tables I and II, the equilibrium compositions obtained by these two methods are similar. Furthermore, these equilibrium compositions are similar to the miscibility window obtained from Figure 1. The average value of ω_1' is about 0.97. When the T_g (PPE) line as a function of overall composition in Figure 4 was drawn, this result was taken into consideration. Thus, on this PPE-rich phase T_g line an arrow shows the boundary between the miscible and immiscible regions.

The Flory–Huggins equation was developed for systems at equilibrium. From the theory, the chemical potential of component in a mixture, as discussed by Tompa,[9] is obtained as a partial derivative of Gibbs free energy with respect to n_i, the number of moles of the ith component:

$$\frac{\Delta \mu_1}{RT} = \ln \phi_1 + \left(1 - \frac{m_1}{m_2}\right) \phi_2 + m_1 \chi_{12} \phi_2^2 \tag{5}$$

$$\frac{\Delta \mu_2}{RT} = \ln \phi_2 + \left(1 - \frac{m_2}{m_1}\right) \phi_1 + m_2 \chi_{12} \phi_1^2 \tag{6}$$

At equilibrium, the chemical potential of each component is the same in both phases. Denoting the PPE-rich phase and SAN-rich phase in equilibrium by $'$ and $''$,

$$\Delta \mu_1' = \Delta \mu_1'' \tag{7}$$

$$\Delta \mu_2' = \Delta \mu_2'' \tag{8}$$

Equation (7) yields

$$\chi_{12} = \frac{\ln \dfrac{\phi_1''}{\phi_1'} + \left(1 - \dfrac{m_1}{m_2}\right)(\phi_2'' - \phi_2')}{m_1(\phi_2'^2 - \phi_2''^2)}. \tag{9}$$

Similarly, eq. (8) yields

$$\chi_{12} = \frac{\ln \dfrac{\phi_2''}{\phi_2'} + \left(1 - \dfrac{m_2}{m_1}\right)(\phi_1'' - \phi_1')}{m_2(\phi_1'^2 - \phi_1''^2)}. \tag{10}$$

Although eqs. (7) and (8) should give the same value of χ_{12}, the inherent complexity of the equation involved leads to slightly different values. The last two columns of Table I show that the interaction parameter calculated from

Table II T_g, Composition of Immisible Phases in Equilibrium Calculated Using Fox Equation, and Interaction Parameter of PPE(1)/SAN(2) Blends

Blend (Wt. SAN)	T_g (PPE)	T_g (SAN)	ω_1'	ϕ_1'	ω_1''	ϕ_1''	Interaction Parameter [eq. (9)]	Interaction Parameter [eq. (10)]
0.00	217.80							
0.10	215.00	113.50	0.9801	0.9824	0.0636	0.0714	0.0150	0.0096
0.20	215.20	113.70	0.9815	0.9836	0.0659	0.0739	0.0148	0.0096
0.30	216.00	114.00	0.9872	0.9887	0.0693	0.0777	0.0145	0.0099
0.40	215.10	112.90	0.9808	0.9830	0.0568	0.0638	0.0156	0.0096
0.50	214.70	113.20	0.9779	0.9805	0.0602	0.0676	0.0153	0.0095
0.60	214.20	112.60	0.9744	0.9773	0.0533	0.0599	0.0159	0.0095
0.70	215.00	112.50	0.9801	0.9824	0.0522	0.0587	0.0160	0.0097
0.80		112.00						
0.90		112.10						
0.91		111.00						
0.93		112.00						
0.94		112.00						
0.95		111.00						
0.97		110.50						
0.98		110.00						
0.99		110.00						
1.00		108.00						

these equations and eq. (2) are in the vicinity of 0.012. Table II shows the similar interaction parameter as the equilibrium compositions calculated by Fox equation are similar to those by eq. (2).

CONCLUSIONS

PPE/SAN was found to be a partially miscible system. SAN dissolves in the PPE to about 3% and PPE dissolves in SAN to about 6%. In the miscible regions, T_g (PPE) decreased with an increase of SAN concentration and T_g (SAN) increased with an increase of PPE. In the immiscible region, the blends were assumed to reach equilibrium upon kneading. In this immiscible region of the blends, two T_gs were observed: T_g (PPE), associated with the PPE-rich phase, and T_g (SAN), associated with the SAN-rich phase. Polymer–polymer interaction parameter of an PPE/SAN system where SAN contains 25% acrylonitrile has been found to be about 0.012.

References

1. J. Stoelting, F. E. Karasz, and W. J. Macknight, *Polym. Eng. Sci.*, **10**, 133 (1970).

2. A. R. Schultz and B. M. Gendron, *J. Appl. Polym. Sci.*, **16**, 461 (1972).
3. W. M. Prest, Jr. and R. S. Porter, *J. Polym. Sci.*, **16**, 461 (1972).
4. R. P. Kambour, J. T. Bendler, and R. C. Bopp, *Macromolecules*, **16**, 753 (1983).
5. K. Kressler and H. W. Krammer, *Acta Polymerica*, **38**, 600 (1987).
6. W. N. Kim and C. M. Burns, *Macromolecules*, **20**, 1876 (1987).
7. L. A. Wood, *J. Polym. Soc.*, **2**(1), 123 (1956).
8. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, chap. 12.
9. H. Tompa, *Trans. Faraday Soc.*, **45**, 1142 (1949); *Polymer Solutions*, Butterworth, London, 1956, chaps. 4 and 7.

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