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Study of Interaction Parameters of Phase-Separated Polymer Blends by Differential Scanning Calorimetry

HSINJIN YANG,* SHARON RICCI, AND
MAUREEN COLLINS

Electronic Imaging Research Laboratories,
Eastman Kodak Company, Rochester, New York 14650-2135

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1. Introduction

In recent years, polymer blends and composites have been very active areas in both academic and industrial communities. The degree of miscibility of polymer blends can provide important information to design desired structures and has usually been understood in terms of the Flory–Huggins interaction parameter (χ) between component polymers. Methods for determining the χ value in miscible blends have been studied widely.[1,2] Several techniques have been applied such as small angle neutron (SANS) and X-ray (SAXS) scattering,[3] inverse gas chromatography,[4] and melting point depression.[5] Only a few methods have been developed to determine the χ value for phase-separated polymer blend systems, and most of these are ternary solution methods.[6] Differential scanning calorimetry (DSC) may be the most convenient and inexpensive method to determine the χ value of phase-separated polymer blends in the solid state. This technique has been used extensively for the blends of polystyrene (PS)/Bisphenol A polycarbonate (PC),[7] PC/poly(methyl methacrylate) (PMMA),[8] PS/PMMA,[9] and PC/poly(ethylene terephthalate)[10] by Burns et al. The χ value can be calculated using DSC data from the experimental value of the glass transition temperature (T_g) and/or heat capacity increment (ΔC_p).

In this paper, DSC is applied to obtain χ values of partially miscible polymer blends, PS/poly(α-methylstyrene) (PαMS). The reasons for chosing the above blends are (a) both polymers have narrow molecular weight distribution, (b) a variety of molecular weights are available, (c) their miscibility is very dependent on the molecular weight,[11,12] (d) the χ value has been measured by SANS.[13] The χ results of the blends are also compared with SANS data.

2. Theoretical Background

Burns and Kim have used the DSC technique to determine the χ value for some phase-separated polymer blends[7-10] from the T_g data. In their papers, they have applied the Flory–Huggins (F–H)[14,15] theory of polymer solutions, and the Scott[16] and Tompa[17] extensive F–H theory on the mixtures of polymers with and without added solvent to describe the determination of χ values for phase-separated polymer blends from the phase compositions.[7-10] The phase compositions can be obtained from the measured T_g data. The χ equations can then be derived as a function of phase compositions[7-10,14-17] with the consideration of size difference between the repeating unit of the components[18]

$$\tilde{\chi} = \chi/v_0 = \frac{\ln(\phi_1^{\,b}/\phi_1^{\,a}) + [1 - (y_1v_1/y_2v_2)](\phi_2^{\,b} - \phi_2^{\,a})}{y_1v_1[(\phi_2^{\,a})^2 - (\phi_2^{\,b})^2]} \qquad (1)$$

or

$$\tilde{\chi} = \chi/v_0 = \frac{\ln(\phi_2^{\,b}/\phi_2^{\,a}) + [1 - (y_2v_2/y_1v_1)](\phi_1^{\,b} - \phi_1^{\,a})}{y_2v_2[(\phi_1^{\,a})^2 - (\phi_1^{\,b})^2]} \qquad (2)$$

where ϕ_i and y_i are the volume fraction and degree of polymerization of component polymer i, respectively, v_i is the molar volume of a repeating unit of component i and v_0 is the reference volume of a lattice. It is worth mentioning here that χ is usually found to be composition-dependent.[3] The detailed physical significance of the χ values obtained from different methods and their composition dependence have been discussed by Sanchez.[18] Therefore, χ can be calculated according to eq 1 or eq 2 if the phase compositions, $\phi_{i,j}^{\,a}$ and $\phi_{i,j}^{\,b}$, are known, where a and b denote two phases. The latter values can be determined from the T_g data of blends, as described in the text that follows.

Table I
Characteristics of Polymers Used in This Study

	density, g/cm^3	ΔC_p, J/(g °C)	M_w/M_n
PS	1.048	0.29	<1.06
PαMS	1.065	0.22	<1.06

The interaction parameter at the spinodal point,[14-17] χ_s, is

$$\tilde{\chi}_s = \chi_s/v_0 = \frac{1}{2}\left(\frac{1}{y_1v_1\phi_1} + \frac{1}{y_2v_2\phi_2}\right) \qquad (3)$$

and the interaction parameter at the critical point,[14-17] χ_c, is

$$\tilde{\chi}_c = \chi_c/v_0 = \frac{1}{2}\left(\frac{1}{(y_1v_1)^{1/2}} + \frac{1}{(y_2v_2)^{1/2}}\right)^2 \qquad (4)$$

As shown in eq 4, χ_c can be derived easily from the degree of polymerization and the repeating unit volume of the components. This value can serve as a criterion for predicting phase stability or phase separation of a blend if their χ value is determined. In other words, the blend can form a single and stable phase if $\chi < \chi_c$ or it will be phase-separated if $\chi > \chi_c$.

3. Experimental Section

The characteristics of polymers used in this study are listed in Table I. The polymers were purchased from either Polymer Labs or Pressure Chemical Co.

A desired weight ratio of PS/PαMS blends was mixed in toluene solution and then precipitated from methanol. The samples were dried in a vacuum oven at 50 °C for several days.

Sample weight of 7–15 mg and heating rate of 10 °C/min were used on the Perkin-Elmer DSC-7 measurements. T_g is defined as the midpoint of the glass transition.

4. Results and Discussion

The phase separation behavior of PS/PαMS blends as a function of molecular weight has been studied and discussed by Wunderlich et al.[11] and Cowie et al.[12] using the DSC technique. Figure 1 shows our DSC results of 50/50 wt % PαMS (M_w = 50 000) blending with various molecular weights of PS. These data show that a single T_g is obtained from lower M_w, a single and broader T_g for intermediate M_w, and a two T_g's for higher M_w. Apparently, the miscibility of this polymer blend is very molecular weight dependent. Figure 2 shows the DSC results at different compositions for PαMS (50 K)/PS (13.5 K). The values of T_g determined from these data are listed in

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* To whom correspondence should be addressed.

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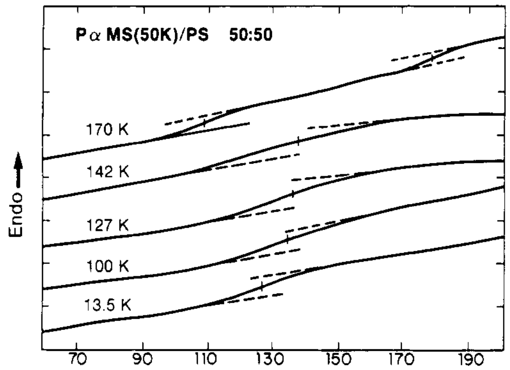

Figure 1. DSC second scan of PS/PαMS (M_w = 50 000) 50/50 wt % blends as a function of PS molecular weight indicated on each curve.

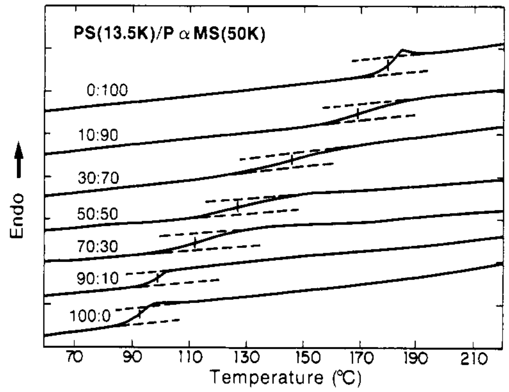

Figure 2. DSC second scan of PS (M_w = 13 500)/PαMS (M_w = 50 000) for all ranges of compositions.

Table II
T_g Results for the Miscible Case of PS (13.5 K)/PαMS (50 K) Blends

PS/PαMS	T_g,[a] °C	PS/PαMS	T_g,[a] °C
0/100	180.1	70/30	110.8
10/90	169.4	90/10	99.0
30/70	146.5	100/0	92.7
50/50	126.6		

[a] ±0.5.

Table II. It can be seen that a single T_g was observed for all compositions, indicating a miscible system. The T_g behavior of miscible polymer blends can usually be described by the following equations:

(a) Gordon–Taylor (G–T) equation[19]

$$T_{gB} = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} \quad \text{where } k = \Delta\alpha_2/\Delta\alpha_1 \tag{5}$$

(b) Fox equation[20]

$$\frac{1}{T_{gB}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{6}$$

(c) Couchman equation[21]

$$\ln T_{gB} = \frac{W_1 \Delta C_{p1} \ln T_{g1} + W_2 \Delta C_{p2} \ln T_{g2}}{W_1 \Delta C_{p1} + W_2 \Delta C_{p2}} \tag{7}$$

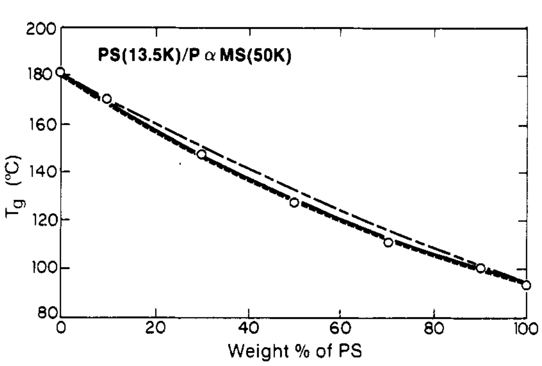

Figure 3. T_g versus composition of PS for miscible case of PS (M_w = 13 500)/PαMS (M_w = 50 000). The T_g curves were fitted by the Fox equation (- - -), the Couchman equation (—), and the Gordon–Taylor equation (- - -).

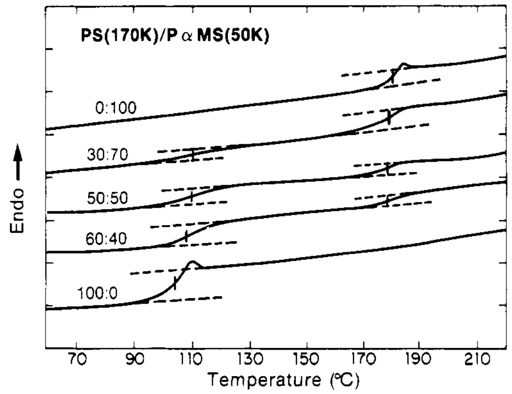

Figure 4. DSC second scan of PS (M_w = 170 000), PαMS (M_w = 50 000), and their blends with compositions of (PS/PαMS) 30/70, 50/50, and 60/40.

where T_{gi} and W_i are the T_g and weight ratio of the component polymer i, respectively, T_{gB} is the T_g of the polymer blend, and $\Delta\alpha_i$ is the thermal expansion coefficient of the component polymer i. Figure 3 demonstrates the fit of the T_g data of the miscible blend PS/PαMS with the above three equations. It is seen that both the G–T equation with k = 1.5 and the Couchman equation can appropriately describe the T_g behavior of PS/PαMS blends. These equations were then used to determine the phase composition for the phase-separated PS/PαMS blends.

It is reasonable to assume that each of these two phases, e.g., phase "a" (the high-T_g PαMS-rich phase) and phase "b" (the low-T_g PS-rich phase), can be described by either the G–T equation, k = 1.5, or the Couchman equation. Therefore, the phase composition of component 1 in phase a can be obtained from a rearrangement of the G–T equation

$$W_{1a} = \frac{-k(T_{gB}{}^{a} - T_{g2})}{(T_{gB}{}^{a} - T_{g1}) - k(T_{gB}{}^{a} - T_{g2})} \tag{8}$$

or from a rearrangement of the Couchman equation

$$W_{1a} = \frac{\Delta C_{p2}(\ln T_{gB}{}^{a} - \ln T_{g2})}{\Delta C_{p1}(\ln T_{g1} - \ln T_{gB}{}^{a}) + \Delta C_{p2}(\ln T_{gB}{}^{a} - \ln T_{g2})} \tag{9}$$

and $W_{2a} = 1 - W_{1a}$. A similar calculation for phase b can be made. Therefore, the phase compositions of PS/PαMS blends can be determined by either eq 8 or eq 9 from the T_g data. For the blend of PαMS and higher M_w of PS (170 K), two T_g's are seen for all ranges of compositions as shown in Figure 4, indicating the system is not miscible. The T_g results are listed in Table III, and therefore, the phase compositions of two phases (a and b) can be

Table III
T_g Results for the Phase-Separated Case of PS (170 K)/PαMS (50 K) Blends

PS/PαMS	T_g,[a] °C	PS/PαMS	T_g,[a] °C
100/0	104.0	60/40	110.1; 179.0
30/70	106.8; 178.1	0/100	180.1
50/50	109.8; 178.0		

[a] ±0.5.

Table IV
χ Results of PS (170 K)/PαMS (50 K) Blends from DSC Measurements

PS/PαMS	ϕ_{1a}	ϕ_{1b}	$10^5\bar{\chi}$	$10^3\chi$	$10^3\chi_S$
A. G–T Equation, $k = 1.5$ [$\chi_C = 2.5 \times 10^{-3}$]					
30/70	0.982	0.054	4.7	4.9	2.7
50/50	0.981	0.110	4.1	4.3	2.8
60/40	0.992	0.116	4.3	4.5	3.3
B. Couchman Equation					
30/70	0.984	0.063	4.6	4.8	2.7
50/50	0.981	0.126	4.0	4.2	2.8
60/40	0.992	0.132	4.2	4.4	3.3

Table V
χ Data from SANS Measurements[a,b]

d-PS/PαMS	$10^3\chi$
20/80	4.9
40/60	4.5

[a] Gallot et al., 1989. [b] PS: M_w = 37 700, M_w/M_n = 1.11. PαMS: M_w = 64 300, M_w/M_n = 1.15.

calculated according to eq 8 or eq 9. The results of the calculation are given in Table IV. We can then estimate χ in terms of eq 1 or eq 2, provided that the system is at equlibrium or nearly so. The average χ data obtained from eq 1 or eq 2 were tabulated in Table IV. The χ value for the PS/PαMS blend is (4.2–4.9) × 10^{-3} and is only slightly composition-dependent. The χ values in Table IV were calculated by assuming that $v_0 = (v_1 v_2)^{1/2}$ or $1/v_0 = \phi_1/v_1 + \phi_2/v_2$[11] ($v_0 = 105$ cm^3/mol). The χ_s and χ_c values were also calculated by eqs 5 and 6, respectively, and the results are shown in Table IV.

The χ values of the PS/PαMS blend have also been measured by Gallot et al.[13] applying the SANS technique, and their results are given in Table V. It should be mentioned here that SANS can only be employed in the blends that are located in the one-phase region of the miscibility diagram. Comparing the results given in Table IV and Table V, we note that the χ values of the PS/PαMS blend measured by DSC and SANS are very consistent. Therefore, DSC can be an effective technique to measure χ especially for partially miscible or phase-separated polymer blends in which SANS cannot be applied.

5. Conclusions

Differential scanning calorimetry (DSC) has been successfully applied to obtain the χ value of PS/PαMS. The miscibility of PS/PαMS is indeed molecular weight dependent. For the low MW case, e.g., PS (13.5 K)/PαMS (50 K), the blend shows a single T_g behavior for all ranges of compositions. The T_g behavior is well described by the Gordon–Taylor equation with $K = 1.5$ and the Couchman equation. For the high MW case, e.g., PS (170 K)/PαMS (50 K), the blend exhibits two T_g's for all ranges of compositions indicating phase separation. The phase compositions and χ values have the been obtained from the T_g results.

The χ value for the PS/PαMS blend is ~4.5 × 10^{-3} from DSC measurements and is not significantly dependent on blend composition. The χ vs composition results are coincident with the data of Gallot et al. measured by small angle neutron scattering. It is noted that SANS can be only measured in the one-phase regions of the polymer blends. Therefore, DSC can be an effective technique to measure χ for partially miscible or phase-separated polymer blends.

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Registry No. PS (homopolymer), 9003-53-6; PαMS (homopolymer), 25014-31-7.