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Thermodynamic study of glass transitions in miscible polymer blends

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Contemporary theoretical considerations of glass transitions in miscible binary polymer blends give the thermodynamic functions associated with the excess properties of mixing in liquid and glass states. A striking feature of the present analysis is that fewer assumptions are involved in the derivations. The values of the new parameters are reported for a number of polymer pairs, representing various types of intermolecular interactions. It is demonstrated that the enthalpy and entropy of mixing are virtually discontinuous at the glass transition temperature of the blend, T_{gb}, particularly for the cases of large deviations of T_{gb} from the weight-average values. In addition, the difference between the polymer–polymer interaction parameters of the blend in the liquid and glassy states, $\Delta\chi$, is indeed linearly related to the reciprocal of T_{gb}. Other implications of the results are discussed.

(Keywords: glass transition; thermodynamic; miscible blends)

INTRODUCTION

The phase behaviour of polymeric systems may be studied by means of the glass transition temperature, T_g, which is readily accessible by a variety of experimental techniques, such as differential scanning calorimetry (d.s.c.). Here we are particularly concerned with the miscible binary polymer blends that exhibit a single T_g lying between the T_gs of the two components. On the basis of the classical thermodynamic theory, a number of equations have been developed to describe the composition dependence of this characteristic parameter satisfactorily[1–5].

The miscibility of polymer blends is generally believed to originate from the specific interactions between polymers. Hence, it is desirable to know the strength of these intermolecular forces. In this connection, there has recently been immense interest in probing the polymer–polymer interaction parameter, χ, as well as the excess properties of mixing from the relevant d.s.c. data of these systems[6–9].

The present work focuses primarily on the above thermodynamic quantities associated with the glass transitions. Values of these parameters will be estimated for some representative systems. The results are useful for various purposes to be addressed below.

THEORY

Basically, the following analyses follow the thermodynamic approach for the regular solutions as practised by other workers[1,2,4,9].

The enthalpy of a mixture, H_{12}, comprising n_1 moles of polymer P_1 and n_2 moles of polymer P_2 is given by

$$H_{12} = n_1 H_1 + n_2 H_2 + \Delta H_m \tag{1}$$

where H_1 and H_2 are the molar enthalpies of P_1 and P_2 respectively, and ΔH_m is the enthalpy of mixing. Equation (1) is applicable to both the liquid and equilibrium glassy states, respectively designated by the superscripts l and g, which can be appended to any functions of interest hereafter. At the temperature T, the molar enthalpy of polymer i having glass transition temperature T_{gi} in the liquid state $H_i^l(T)$, is given by

$$H_i^l(T) = H_i^l(T_{gi}) + \int_{T_{gi}}^{T} \bar{C}_{pi}^l \, dT \tag{2}$$

where the subscript i ($i = 1, 2$) serves to identify the parameter pertaining to the component polymer i hereafter, and $\bar{C}_p$ is the molar heat capacity at constant pressure. An analogous expression can be readily written for the polymer i in the glassy state. By virtue of Ehrenfest's theory of second-order transition[10], we have $H_i^l(T_{gi}) = H_i^g(T_{gi})$, which enables us to obtain

$$H_i^l(T) - H_i^g(T) = \int_{T_{gi}}^{T} \Delta\bar{C}_{pi} \, dT \tag{3}$$

where

$$\Delta\bar{C}_{pi} = \bar{C}_{pi}^l - \bar{C}_{pi}^g \tag{3a}$$

Analogously, the function H_{12} is also continuous at the T_g of the miscible polymer blend $(n_1P_1 + n_2P_2)$ designated by T_{gb}. This means that $H_{12}^l(T_{gb}) = H_{12}^g(T_{gb})$. Combining the previous condition and substituting $\Delta\bar{C}_{pi}$ by the corresponding specific heat capacity increment, ΔC_{pi}, equation (1) leads to

$$-\Delta H^E(T_{gb}) = w_1 \int_{T_{g1}}^{T_{gb}} \Delta C_{p1} \, dT + w_2 \int_{T_{g2}}^{T_{gb}} \Delta C_{p2} \, dT \tag{4}$$

where $T_{g1} < T_{gb} < T_{g2}$, w_i is the weight fraction of component i, and ΔH^E is the difference between the liquid and glass enthalpies of mixing defined by

$$\Delta H^{E} = (\Delta H^{l}_{m} - \Delta H^{g}_{m})/W \qquad (4a)$$

with W being the total weight of the polymer blend.

By assuming the continuity of the entropy of the blend $(n_1P_1 + n_2P_2)$ at T_{gb}, Couchman and others[3,9] have offered an expression for the difference between the liquid and glass entropies of mixing, ΔS^{E} given by

$$-\Delta S^{E}(T_{gb}) = w_1 \int_{T_{g1}}^{T_{gb}} \Delta C_{p1}\,\mathrm{d}\ln T + w_2 \int_{T_{g2}}^{T_{gb}} \Delta C_{p2}\,\mathrm{d}\ln T \qquad (5)$$

where

$$\Delta S^{E} = (\Delta S^{l}_{m} - \Delta S^{g}_{m})/W \qquad (5a)$$

with ΔS_m being the entropy of mixing. Combining equations (4) and (5) yields the corresponding function in terms of the free energy of mixing, ΔG_m at T_{gb}, i.e.

$$\Delta G^{E} = \Delta H^{E} - T_{gb}\Delta S^{E} \qquad (6)$$

where

$$\Delta G^{E} = (\Delta G^{l}_{m} - \Delta G^{g}_{m})/W \qquad (6a)$$

Clearly, it is vital to know the temperature dependence of ΔC_{pi} for the present analyses.

According to the Flory–Huggins lattice model of polymer solutions[11], the polymer–polymer interaction parameter, χ, is defined by

$$\Delta H_m = \chi RT\phi_1\phi_2 V/V_s \qquad (7)$$

where R is the gas constant, ϕ is the volume fraction, V is the total volume and V_s is the molar volume of polymer segment (lattice). It follows that equation (4a) becomes

$$\Delta H^{E}(T_{gb}) = RT_{gb}\phi_1\phi_2(V/WV_s)\Delta\chi \qquad (8)$$

where

$$\Delta\chi = \chi^{l}(T_{gb}) - \chi^{g}(T_{gb}) \qquad (8a)$$

By appropriate substitutions, equations (4) and (8) result in

$$-RT_{gb}Fw_1w_2\Delta\chi = w_1 \int_{T_{g1}}^{T_{gb}} \Delta C_{p1}\,\mathrm{d}T + w_2 \int_{T_{g2}}^{T_{gb}} \Delta C_{p2}\,\mathrm{d}T \qquad (9)$$

where

$$F = \frac{(w_1/M_1 + w_2/M_2)}{\rho_1\rho_2(w_1/\rho_1 + w_2/\rho_2)^2} \qquad (9a)$$

with M_i and ρ_i $(i = 1, 2)$ being respectively the molecular weight of the repeat unit and density of polymer i. Indeed, equation (9), which facilitates the estimation of $\Delta\chi$, is given in a form symmetrical about 1 and 2. It has been proposed that the parameter χ consists of two basic thermodynamic terms[11,12]. Accordingly, equation (8a) renders

$$\Delta\chi = z(\Delta e_h - T_{gb}\Delta e_s)/kT_{gb} \qquad (10)$$

where z is the lattice coordination number, k is the Boltzmann constant, and

$$\Delta e_h = \Delta w^{l}_{h} - \Delta w^{g}_{h} \qquad (10a)$$

$$\Delta e_s = \Delta w^{l}_{s} - \Delta w^{g}_{s} \qquad (10b)$$

with Δw_h and $T_{gb}\Delta w_s$ being respectively the enthalpic and entropic contributions to the exchange interaction energy between the polymer segments. Hence, a plot of $\Delta\chi$ against $1/T_{gb}$ would result in a straight line with the gradient and intercept equal to $z\Delta e_h/k$ and $-z\Delta e_s/k$, respectively.

RESULTS AND DISCUSSION

The specific heat capacity increment is assumed to be a linear function of T below and above the T_g of the polymer, given by

$$\Delta C_p = a + bT \qquad (11)$$

where a and b are the coefficients. *Table 1* displays the values of a and b for a number of polymers together with their abbreviations. This information is either collected from the literature[9–13], or obtained by means of the group contribution method[13] based on 298 K. The polymers are selected in order to form various miscible polymer blends. Hereafter, a miscible polymer blend is listed as polymer 1/polymer 2.

By studying the literature data obtained from various sources, Schneider and Di Marzio have established the empirical relationships between T_g and composition for two series of miscible blends that have been investigated extensively[14]. These are the Fox expression for PS/PPO,

Table 1 Specific heat capacity increments, ΔC_p, for some polymers

No.	Polymer (abbreviation)	$\Delta C_p = a + bT$ a (J g^{-1} K^{-1})	 $-b \times 10^3$ (J g^{-1} K^{-2})
1	Polystyrene (PS)	1.036	1.96
2	Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)	0.978	1.58
3	*Cis*-1,4-polyisoprene (PIP)	0.726	1.30
4	Poly(vinyl ethylene) (PVE)	1.113	2.46
5	Poly(vinyl chloride) (PVC)	0.974	1.87
6	Poly(ethyl methacrylate) (PEMA)	0.850	1.63
7	Poly(*N,N*-dimethyl acrylamide) (PDMA)	1.117[a]	1.95[a]
8	Poly(4-hydroxyl styrene) (PHOS)	0.995[a]	1.33[a]
9	Poly(vinyl methyl ether) (PVME)	1.023[a]	2.02[a]
10	Poly(methyl methacrylate) (PMMA)	0.849	1.44
11	Styrene/maleic anhydride (MA) copolymer containing 8 wt% MA (SMA8)	1.041[a]	1.85[a]

[a] Estimated by the contribution method as outlined in ref. 13

and a third-power series in blend composition for PVME/PS. In an even more interesting study, Roland and Trask have observed that in the absence of specific interactions, PIP mixes with PVE to form almost ideal mixtures[15,16]. This is ascribed to the small but significant change in the entropy of mixing. The T_g of this non-polar system follows a Couchman's equation[15]. It is noted that all the foregoing single-phase blends exhibit negative values of ΔT, defined as the deviation of T_g from the weight additivity rule, given by

$$\Delta T = T_{gb} - (w_1 T_{g1} + w_2 T_{g2}) \qquad (12)$$

Three other polymeric systems are particularly chosen below to highlight a different situation in which positive deviations of T_g (i.e. $\Delta T > 0$) are encountered. It has been shown that blending of PMMA with a series of styrene/maleic anhydride (MA) copolymers seems to result in a 'miscibility window'[17]. At 8% MA, the miscibility is evidenced by the fact that the PMMA/SMA8 blends demonstrate a distinct single T_g over the whole range of blend compositions. The phase behaviour of the miscible PVC/PEMA has been reported by Perrin and Prud'homme[18], who have found the T_g–composition curve best reproduced by the Kwei equation[19], which implies the presence of strong intermolecular interactions. Recently, Wang *et al.*[20] have presented the glass transitions of polymer complexes resulting from the strong hydrogen bonds. Notably, the values of T_g for the precipitates prepared by mixing PDMA with PHOS is dioxane are strikingly higher than those of the two components at some intermediate blend compositions. All the T_g data required for the present work are published in the literature cited above.

Table 2 Values of solubility parameter difference, $|\Delta\delta|^a$, for various miscible polymer blends

No.	Polymer blend	$\lvert\Delta\delta\rvert$ ((J ml^{-1})$^{1/2}$)	Type of intermolecular interactions
1	PS/PPO	0.6^b	Dipole–dipole
2	PVME/PS	1.1^c	Dipole–dipole
3	PIP/PVE	0^d	Dispersive forces
4	PMMA/SMA8	1.6^e	Weak hydrogen bonds
5	PVC/PEMA	1.5^f	Weak hydrogen bonds
6	PDMA/PHOS	6.3^g	Strong hydrogen bonds

[a] $\Delta\delta = \delta_1 - \delta_2$, where δ_1 and δ_2 are the solubility parameters of polymers 1 and 2, respectively

[b] Data for δ_1 and δ_2 are obtained respectively from refs 25 and 26

[c] Values of δ_2 are estimated by the group contribution method[21]

[d] See refs 15 and 16

[e] Data for δ_1 and δ_2 are obtained from ref. 25, and the group contribution method[21], respectively

[f] Data are obtained from ref. 26

[g] The value of δ_1 is obtained from ref. 26, whereas that of δ_2 is estimated by the Fedors' group contribution method[13]

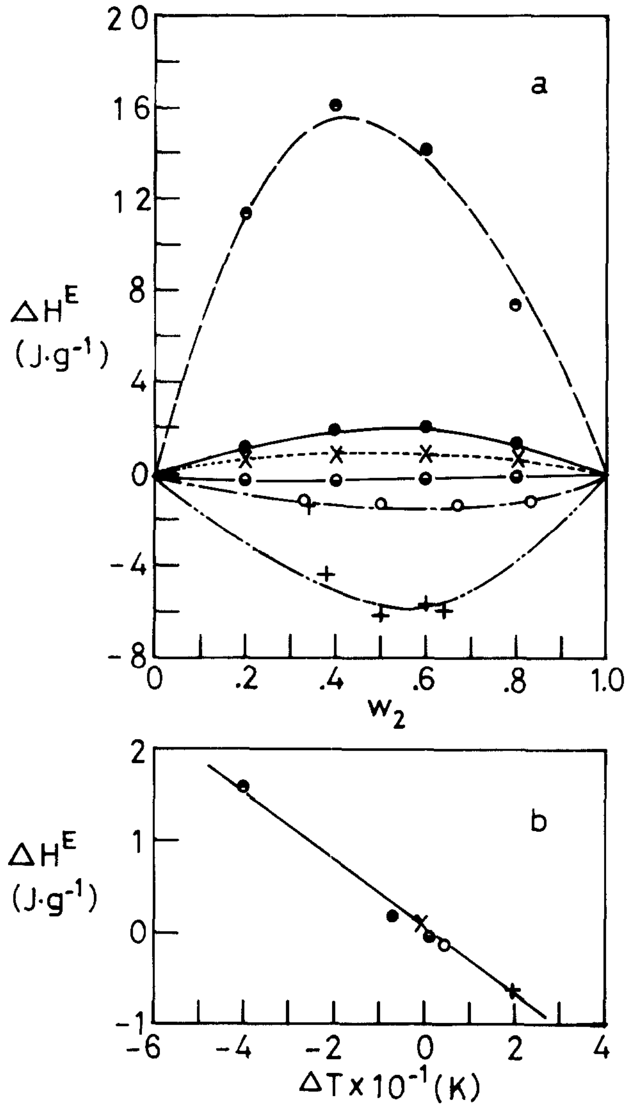

Figure 1 (a) Plots of ΔH^E (T_{gb}) against w_2 for various polymer blends: (●) PS/PPO; (◓) PVME/PS; (×) PIP/PVE; (◒) PMMA/SMA8; (○) PVC/PEMA; (+) PDMA/PHOS. (b) Linear plot of ΔH^E (T_{gb}) against ΔT for the above polymer blends. Herein, only the highest/lowest observed values of ΔH^E (T_{gb}) for the polymer blends, represented by the same symbols as above, are used

Equation (4) is employed to compute the ΔH^E as a function of weight fraction, w_2. The results obtained for the six miscible blends are shown in *Figure 1a*, displaying the values of ΔH^E varying from -6 to 16 J g^{-1}. Recently, Coleman *et al.* have proposed a practical means to predict the polymer miscibility by simply matching the solubility parameters, δ, of the two polymers[21]. According to this scheme, the present systems of interest can be approximately categorized into four distinct types in terms of the strength of intermolecular interactions as shown in *Table 2*, which also lists the values of the solubility parameter difference, $|\Delta\delta|$. Clearly, *Figure 1a* shows that the weak favourable interactions result in positive ΔH^E, whereas the relatively strong hydrogen bonds lead to negative ΔH^E. However, no simple correlations between ΔH^E and $|\Delta\delta|$ are apparent. In contrast, *Figure 1b* offers a linear plot between ΔH^E and ΔT for different systems given in *Figure 1a*, with both variables referring specifically to the observed extreme values. This means that the deviation of T_g from the weight-average value may serve as a good measure of the extent of increase/decrease in the enthalpy of mixing at the glass transition of a miscible polymer blend.

A parallel behaviour is witnessed for these systems in *Figures 2a* and *b*, where the variations of ΔS^E, computed using equation (5), with w_2 and ΔT respectively are depicted. Again, only the maximum/minimum values of ΔS^E are invoked to demonstrate the linearity. More important, *Figures 1a* and *2a* exhibit a common feature for the six polymer systems in that the ΔH^E and ΔS^E are virtually non-zero, particularly for PVME/PS and

PDMA/PHOS. Physically, it reveals the discontinuity of ΔH_m and ΔS_m at T_{gb}. In addition, equation (6) results in only positive ΔG^E, suggesting that there is a gain of ΔG_m through the glass transition process for any one of the foregoing systems.

Assuming that ΔH_m and ΔS_m are continuous at T_{gb}, and ΔC_p is T-independent, Couchman and Karasz[1,3] have converted equations (4) and (5) respectively to

$$T_{gb} = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \tag{13}$$

$$T_{gb} = \exp\left[\frac{w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}}\right] \tag{14}$$

In fact, the foregoing assumptions have been disputed by Goldstein[2] and other workers[9], and totally disagree with the present findings. Despite this, equations (13) and (14) have been widely employed to fit the experimental $T_{gb} - w_2$ data. However, the success of these applications may be grossly fortuitous as elaborated below. By means of the rule of error propagation, equations (13) and (14) yield the uncertainties of T_{gb}, δT_g, given respectively by

$$\delta T_g = 2T_{gb} \ln (T_{gb}) \Delta \tag{15}$$

$$\delta T_g = 2T_{gb} \Delta \tag{16}$$

where Δ is the relative precision of ΔC_p taken as

$$\Delta = \frac{\delta \Delta C_{p1}}{\Delta C_{p1}} = \frac{\delta \Delta C_{p2}}{\Delta C_{p2}} \tag{16a}$$

with $\delta \Delta C_p$ being the uncertainty of ΔC_p. Clearly, equations (15) and (16) indicate that the reliabilities of equations (13) and (14) depend considerably on the accuracy of the ΔC_p data, particularly the former. The impact of this exercise is indeed apparent, as ΔC_p is not a constant *per se*.

Table 3 shows the values of the enthalpic and entropic terms involved in equation (10) for the six miscible polymer blends. Despite the large uncertainties, the results reflect that the changes in Δw_h and Δw_s at T_{gb} between the liquid and glass states are indeed more prominent for the systems involving strong intermolecular interactions (i.e. systems no. 4–6). In addition, it is interesting to note that the ratio $\Delta e_h/\Delta e_s$ is approximately equal to 365 ± 25 K, except for the PS/PPO and PVME/PS blends, where the T_{g1} and T_{g2} are farther apart. No attempts are made to explain these tentative results at this stage, however.

In studying the compositional variation of T_g, Kwei has extended equation (13) by a quadratic term of $q w_1 w_2$ to account for the specific interactions[19]. If ΔC_{p1} and ΔC_{p2} are T-independent, equation (9) readily renders

$$q = \left(\frac{R T_{gb} F}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}}\right) \Delta \chi \tag{17}$$

Hence, the Kwei factor q virtually monitors the difference $\chi^l - \chi^g$ rather than merely characterizing the interaction strength in terms of χ in a single phase[8].

The values of χ^l for PIP/PVE and PS/PPO blends have been determined to be positive and vanishingly

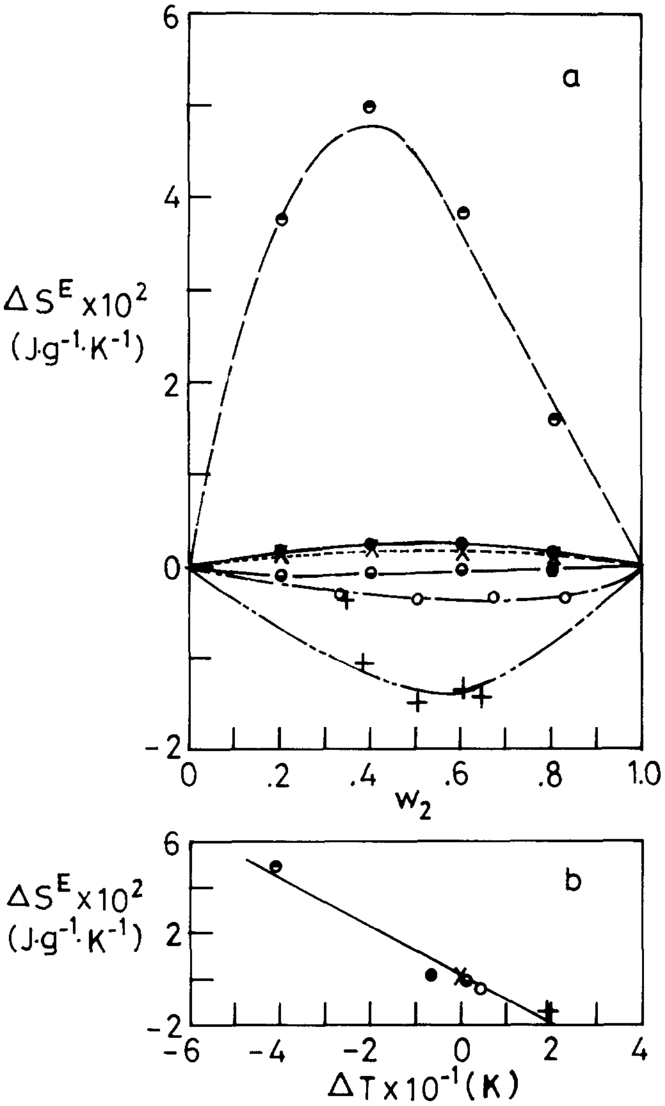

Figure 2 (a) Plots of ΔS^E (T_{gb}) against w_2 for the six miscible polymer blends listed in *Figure 1*. (b) Linear plot of ΔS^E (T_{gb}) against ΔT, for the above systems. Again, only the highest/lowest observed values of ΔS^E (T_{gb}) are used. All symbols are the same as in *Figure 1a*

Table 3 Results of linear least-squares analyses using equation (10)

No.	Polymer blend	$z\Delta e_s/k$	$z\Delta e_h/k$ (K)	r^a
1	PS/PPO	$-(0.31 \pm 0.01^b)$	$-(22 \pm 4^b)$	-0.9671
2	PVME/PS	0.6 ± 0.5	$(7.2 \pm 1.4) \times 10^2$	0.9638
3	PIP/PVE	0.30 ± 0.03	102 ± 8	0.9942
4	PMMA/SMA8	$-(3.6 \pm 1.0)$	$-(1.4 \pm 0.4) \times 10^3$	−0.9317
5	PVC/PEMA	$-(16 \pm 3)$	$-(5.5 \pm 1.1) \times 10^3$	−0.9616
6	PDMA/PHOS	8.7 ± 0.6	$(3.4 \pm 0.3) \times 10^3$	0.9915

[a] Correlation coefficient
[b] Standard deviation

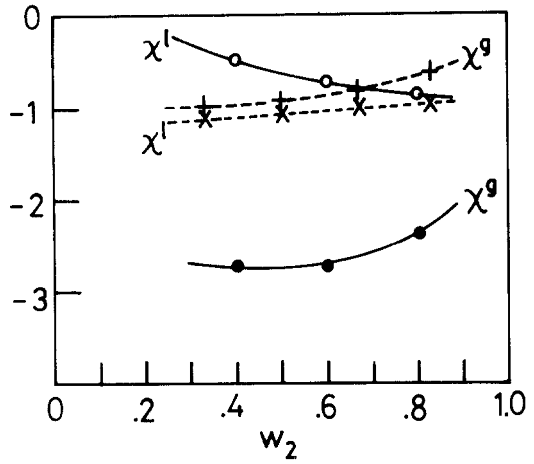

Figure 3 Composition dependence of the liquid and glass interaction parameters χ^l and χ^g for polymer blends: (——, ○, ●) PVME/PS; (- - -, ×, +) PVC/PEMA

small[16,22], resulting in $\chi^g = -\Delta\chi$ equal to ~ -0.10 and -0.25, respectively. On the basis of the binary interaction model after Paul and Barlow for the mixing of polymer and copolymer[23], the interaction energy density, B, is theoretically estimated to be $-0.13\ \mathrm{J\,ml^{-1}}$ at 386.2 K for PMMA/SMA81[17], equivalent to $\chi^l \cong -0.004$ and $\chi^g \cong 0.02$. Unfortunately, the experimental data for χ^l are not available. The same predicament is encountered for the complexes PDMA/PHOS, which, however, have been reported to produce negative excess heat capacities resulting from the hydrogen bonding interactions[20]. As noted, the χ^l values of PVME/PS films have been measured by the vapour sorption method over a range of concentrations[24].

The Flory–Prigogine equation-of-state theory has been applied to interpret the phase behaviour of PVC/PEMA[18]. It can be shown that the parameter B is a sum of a free-volume term B_V and an energy term B_H, i.e.

$$B = B_V + B_H \tag{18}$$

where

$$B_V = P_1^*\left[3\tilde{T}_1 \ln\left(\frac{\tilde{v}_1^{1/3}-1}{\tilde{v}_{12}^{1/2}-1}\right) + \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}_{12}}\right)\right]/\phi_2^2 \tag{18a}$$

$$B_H = \left(\frac{X_{12}}{\tilde{v}_{12}} - TQ_{12}\right)\left(\frac{\theta_2}{\phi_2}\right)^2 \tag{18b}$$

with P^*, $\tilde{T}$, $\tilde{v}$, θ and ϕ being respectively the characteristic pressure, reduced temperature, reduced volume, site fraction and segment fraction, the subscripts 1, 2 and 12 respectively referring to the polymers 1, 2 and their polymer blend, and X_{12} and Q_{12} being the exchange parameters. By definition, we have

$$B = \chi RT/V_1^* \tag{19}$$

where V_1^* is the characteristic molar volume of polymer 1. Since χ^l is only associated with the exchange contact energy, it is not irrational to neglect the effect of free volume in order to obtain

$$\chi^l = B_H V_1^*/RT \tag{20}$$

For this particular polymeric system, X_{12} and Q_{12} are reported to be $-0.37\ \mathrm{J\,ml^{-1}}$ and $-5.08 \times 10^{-4}\ \mathrm{J\,K^{-1}\,ml^{-1}}$, respectively, at 120°C[18]. This information would facilitate the estimation of χ^l.

Figure 3 shows the variations of χ^l and χ^g with the blend concentrations for PVME/PS and PVC/PEMA. Two distinct situations are evidenced herein, namely $\chi^l > \chi^g$ for the former and the reverse for the latter.

Recently, Lu and Weiss[8] have formulated a scheme for estimating χ from the T_g data of miscible polymer blends by modifying the thermodynamic model proposed by Couchman[7]. They considered the difference between the enthalpies of mixing at T_{g1} and T_{g2}, and made, among others, the following approximation written in a form adapted to the present context

$$\Delta H_m^l(T_{g2}) - \Delta H_m^g(T_{g1}) = \chi R\phi_1\phi_2(T_{g2} - T_{g1})V/V_s \tag{21}$$

for $T_{g2} > T_{g1}$. Equation (21) requires that χ is T-independent and $\Delta\chi = 0$. Clearly, both conditions are disproved by the present findings.

CONCLUSIONS

The Ehrenfest model of second-order transitions and the Flory lattice theory of polymer solutions are useful for studying the glass transitions of miscible polymer blends. As a result, the thermodynamic functions ΔH^E, ΔS^E and $\Delta\chi$ are applied respectively to characterize the differences between the liquid and glassy states in terms of the ΔH_m, ΔS_m and χ at the T_{gb}. However, the present approach fails to foresee a practical means for estimating the value of χ exclusively from the d.s.c. data, as claimed recently[8]. Apparently, the signs of ΔH^E and ΔS^E depend greatly on the nature of the intermolecular forces. In addition, linear relationships between various pairs of parameters, including $\Delta H^E - \Delta T$, $\Delta H^E - \Delta T$ and $\Delta\chi - T_{gb}^{-1}$, are established. More important, the functions ΔH_m, ΔS_m and χ are shown to be discontinuous at T_{gb}, particularly for the systems where specific interactions prevail.

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