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Modulated differential scanning calorimetry: 14. Effect of molecular interactions on glass transition behaviour and increment of heat capacity in miscible polymer blends

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Abstract

Molecular interactions in miscible polymer blends influence glass transition (T_g) behaviour and the increment of heat capacity at T_g. Whether the glass transition temperature and the increment of heat capacity versus composition show positive or negative deviations from linearity for blend systems depends on specific molecular interactions. In the non-interacting system, poly(vinyl acetate)/poly(methyl acrylate), the glass transition temperature and the increment of heat capacity show a linear behaviour with composition. Thermodynamic theoretical considerations concerning the non-linear behaviour of the glass transition temperature and the increment of heat capacity with composition in miscible polymer blends are developed in this paper. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Miscibility; Polymer blends; Modulated DSC

1. Introduction

The miscibility and phase behaviour of polymer blends can be studied by determination of the glass transition temperature, T_g. Miscible blends exhibit a single T_g lying between the T_gs of the two components. It is believed that miscibility in polymer blends results from specific interactions between molecules. Hence, it is desirable to know the strength of these intermolecular forces. In this connection, there has recently been immense interest [1–5] in probing the polymer–polymer interaction parameter, χ, as well as the excess properties of mixing from the relevent differential scanning calorimetry (DSC) data.

In studying the variation of T_g with composition, Kwei [6] introduced a quadratic term, $q\omega_1\omega_2$ into the Gordon–Taylor equation in Ref. [7] to account for the specific interactions.

$$T_g = \left(\omega_1 T_{g1} + \omega_2 T_{g2}\right) + q\omega_1\omega_2 \quad (1)$$

ω_1 and ω_2 are the weight fractions and T_{g1} and T_{g2} are the glass transition temperatures for polymer 1 and polymer 2, respectively. The Kwei factor, q, implies [6,8] that different interaction strengths in terms of χ result in different glass transition behaviour. Chow [8] proposed the new concept of non-equilibrium interaction in compatible polymer blends and used it to describe anomalous yield behaviour. Chee [5] indicated that the Kwei factor monitors the difference between interaction parameters in the liquid and the glassy states, rather than merely characterizing the interaction strength in terms of χ in a single phase. Different χ values will result in different mixing enthalpies [9]. It is possible that T_gs and increments of heat capacity, ΔC_p, will show non-linear behaviour in blend systems which exhibit specific interactions, and linear behaviour in the blend systems which exhibit no interactions.

This work will focus on an experimental study of the behaviour of T_g and ΔC_p with composition by means of modulated-temperature DSC (M-TDSC) [10,11] and with thermodynamic quantities associated with the experimental results.

2. Experimental

Samples: Poly(phenylene oxide) (PPO), poly(methyl methacrylate) (PMMA), poly(styrene-co-acrylonitrile) (SAN), poly(methyl acrylate) (PMA) and poly(vinyl acetate) (PVAc) were obtained from Aldrich. Polystyrene (PS) was obtained from BP Chemicals. The characterization data for these polymers are given in Table 1. The average

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Table 1
Sample parameters

Polymer	AN(wt%)	M_w (10^{-5})	M_n (10^{-4})	Blending Solvent
SAN18	17.3	1.65	8.25	Chloroform
SAN30	29.7	1.32	5.38	Chloroform
PMMA		1.98	9.75	Chloroform
PPO		2.40	7.50	Chloroform
PMA		0.40	0.22	Actone
PVAc		0.52	0.25	Actone
PS		2.10	9.30	Chloroform

molecular weights and polydispersities were determined using a Waters model 510 GPC instrument, which was calibrated relative to standard polystyrene samples. The AN contents of the SAN copolymers (SAN18 and SAN30) were determined by 1H nmr spectroscopy using a Jeol FX-100 spectrometer. Films from the miscible blends and the pure constituent polymers were prepared by solvent casting 5 wt% solutions in glass trays. The solvents used for the different polymer pairs are shown in Table 1. After evaporation of these solvents at room temperature, the films were dried at 80°C under vacuum for two weeks. All film samples for M-TDSC measurements were then hot pressed (T_g + 30°C) to achieve flat specimens.

Instrumentation: A TA Instruments modulated-temperature differential scanning calorimeter (M-TDSC-2900) was used. An oscillation amplitude of 1.0°C and oscillation of period 60 seconds were used with a heating rate of 3°C/min. The TA Instruments ''graph ware'' software was used to measure the heat flow, heat capacity and differential of heat capacity. The calorimeter was calibrated with indium and sapphire standards.

3. Results and discussion

Figs. 1–4 show the relationships between measured T_g and composition for PVAc/PMA, PPO/PS, SAN18/PMMA and SAN30/PMMA blends, respectively. Figs. 5–8 show the relationships between measured ΔC_p and composition for the same blends. For comparison, ΔC_p versus composition was determined for physical mixtures [11] of SAN30/PMMA, as shown in Fig. 9. Obviously, for this physical mixture (which is equivalent to an immiscible blend) where there is no segmental interactions, the following relation holds for ΔC_p.

$$\Delta C_p = \omega_1 \Delta C_{p1} + \omega_2 \Delta C_{p2} \quad (2)$$

ΔC_{p1} and ΔC_{p2} are the increments of heat capacity for polymer 1 and polymer 2, respectively.

For the PVAc/PMA blends, which exhibit linear T_g – composition behaviour, the following relation holds,

$$T_g = \omega_1 T_{g1} + \omega_2 T_{g2} \quad (3)$$

Solid-state NMR spectroscopy results showed that no inter-segmental interactions exist in PVAc/PMA blends [12]. This shows that the Kwei factor, as shown in Eq. (1), is equal to zero. In those systems which do exhibit segmental interactions, T_g and ΔC_p versus composition show positive or negative deviations from linear behaviour. Indeed, the Kwei factor is related to such molecular interactions. An interesting observation is that when T_g versus composition shows a negative deviation, ΔC_p versus composition shows a positive deviation from linear

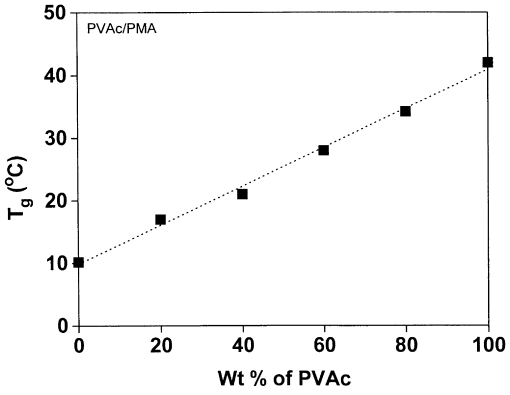

Fig. 1. Glass transition temperature versus composition for PVAc/PMA blends.

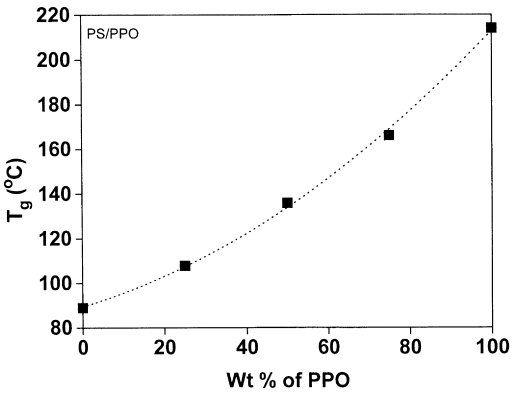

Fig. 2. Glass transition temperature versus composition for PS/PPO blends.

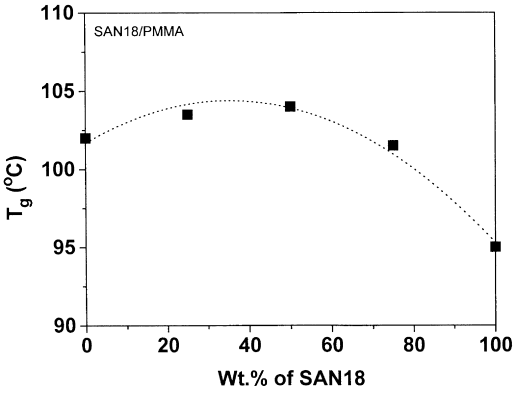

Fig. 3. Glass transition temperature versus composition for SAN18/PMMA blends.

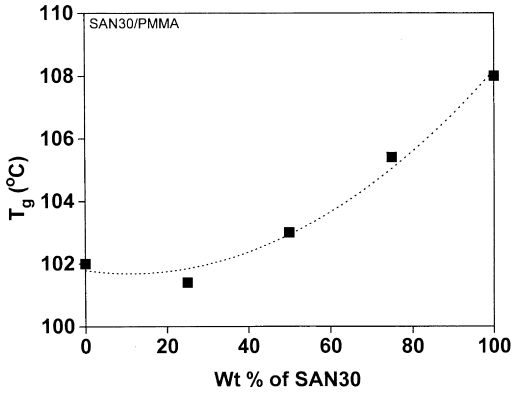

Fig. 4. Glass transition temperature versus composition for SAN30/PMMA blends.

behaviour. For SAN/PMMA blends, with higher AN contents, T_g and ΔC_p versus composition show negative and positive deviations from linearity, respectively. However, at lower AN contents, T_g and ΔC_p versus composition show positive and negative deviations, respectively. It is possible that there is an AN content at which T_g and ΔC_p show linear behaviour with composition change.

The enthalpy of mixing is a much more dominant feature in the phase behaviour of polymer blends than it is for most mixtures of low molecular weight species. This is a result of the large size of polymer molecules and the concomitant lower combinatorial entropy of mixing. This fact is easily seen from the simple Flory–Huggins [9] formula for the free energy of mixing.

$$\Delta G_{mix} = RT(\phi_1 ln\phi_1/V_1 + \phi_2 ln\phi_2/V_2) + \phi_1\phi_2 RT\chi \quad (4)$$

ϕ_i is the component volume fraction and V_i is the component molar volume. The temperature dependence of the heat of mixing for blends is given unambiguously by the excess heat capacity of the blend.

$$(\partial H_{mix}/\partial T)_p = \rho\left(Cp - \omega_1 C_{p1} + \omega_2 C_{p2}\right) \quad (5)$$

The density of the blend, ρ, appears as a factor since the heat capacity is expressed per unit mass, while the heat of mixing is for a unit of volume. According to the concept of non-equilibrium inteaction proposed by Chow [8], the enthalpy of mixing for a binary polymer blend may be represented by a Van Laar relationship [3,5,8,9] at T_g.

$$\Delta H_m^l = \chi^l \phi_1\phi_2 RT_g \qquad \Delta H_m^g = \chi^g \phi_1\phi_2 RT_g \quad (6)$$

χ^l and χ^g are the interaction parameters, and ΔH_m^l and ΔH_m^g are the enthalpies of mixing for the liquid and the glassy states, respectively, at T_g.

Consider that the glass transition is treated as follows as an Ehrenfest transition of approximately second order [3,13] and the two polymers have T_{g1} and T_{g2} ($T_{g1} < T_{g2}$) and the respective molar enthalpies are H_1 and H_2. The molar enthalpy of a mixture of the two polymers is as follows.

$$H_{mix} = m_1 H_1 + m_2 H_2 + \Delta H_m \quad (7)$$

m_1 and m_2 are the molar fractions of polymer 1 and polymer 2, respectively, in the blend. ΔH_m is the excess enthalpy of mixing. Eq. (7) is applicable to both the liquid and equilibrium states. The excess enthalpy of mixing at T_g is given by Eq. (8).

$$\Delta H_m = m_1\Delta H_1 - m_2\Delta H_2 + \chi^l \phi_1\phi_2 RT_g - \chi^g \phi_1\phi_1 RT_g \quad (8)$$

Then, the increment of excess heat capacity at T_g can be shown to be given by the following relation.

$$\delta\Delta C_p = \phi_1\phi_2\left(\chi^l - \chi^g\right)R/\rho \quad (9)$$

$\delta\Delta C_p$ is related to the two strengths of interaction in the liquid and glassy states. Using Eq. (9), our experimental results can be analysed.

When $\chi^l = \chi^g$ or there are no interactions in a miscible blend system,

$$\delta\Delta C_p = 0 \quad (10)$$

and when $\chi^l < 0$, $\chi^g < 0$ and $|\chi^l| < |\chi^g|$,

$$\delta\Delta C_p > 0 \quad (11)$$

and if $\chi^l < 0$, $\chi^g < 0$ and $|\chi^l| < |\chi^g|$ then

$$\delta\Delta C_p < 0 \quad (12)$$

To discuss the χ-dependence of glass transition behaviour versus composition, it is necessary to know the relationship between T_g and χ. Considering the Lu and Weiss work [3,13] and combining Eqs. (7) and (8), an equation for T_g – composition and interaction dependence for polymer blends can be obtained, approximately:

$$T_g = \left(\omega_1 T_{g1} + \omega_2 T_{g2}\right)/ \times\left[1 + \left(\chi^l - \chi^g\right)\phi_1\phi_2 R/\left(\omega_1\Delta C_{p1} + \omega_2\Delta C_{p2}\right)\right] \quad (13)$$

As $\left(\chi^l - \chi^g\right)\phi_1\phi_2 R/\left(\omega_1\Delta C_{p1} + \omega_2\Delta C_{p2}\right) \ll 1$, Eq. (13)

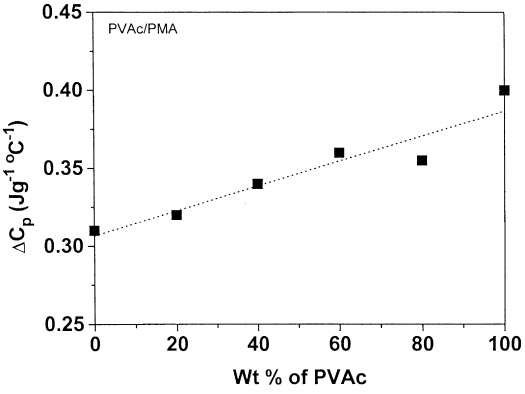

Fig. 5. ΔC_p versus composition for PMA/PVAc blends.

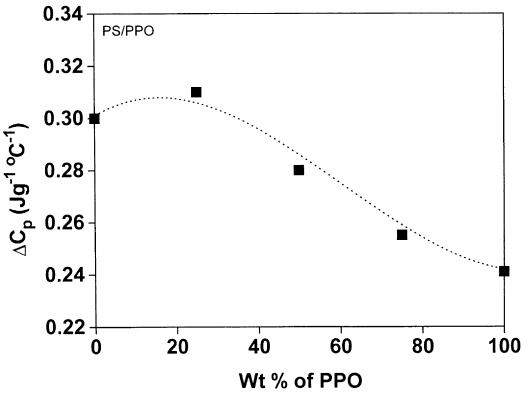

Fig. 6. ΔC_p versus composition for PS/PPO blends.

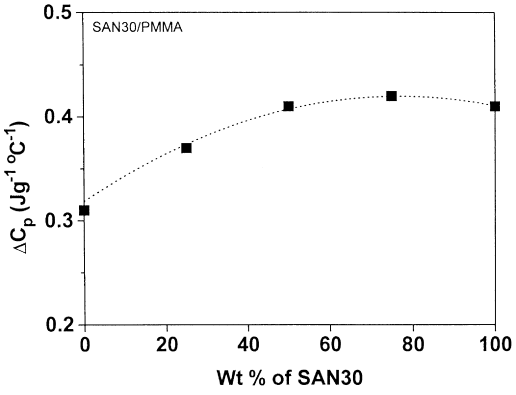

Fig. 8. ΔC_p versus composition for SAN30/PMMA blends.

can be rewritten approximately as follows,

$$T_g = \left[1 - \left(\chi^l - \chi^g\right)\phi_1\phi_2 R/\left(\omega_1\Delta C_{p1} + \omega_2\Delta C_{p2}\right)\right] \times\left(\omega_1 T_{g1} + \omega_2 T_{g2}\right) \quad (14)$$

Thus, it is possible to analyse the interaction dependence of T_g in miscible blends.

1. There will be a positive deviation from linear behaviour when $\chi^l < 0$, $\chi^g < 0$ and $|\chi^l| > |\chi^g|$.
2. There will be a negative deviation from linear behaviour when $\chi^l < 0$, $\chi^g < 0$ and $|\chi^l| < |\chi^g|$.
3. There will be a linear behaviour when $\chi = 0$ or $\chi^l < 0$, $\chi^g < 0$ and $|\chi^l| = |\chi^g|$.

Our experimental results for T_g and ΔC_p prove the above deductions. See Figs. 1–4.

Isasi et al.[14] studied the miscibility of poly(1-vinyl-2-pyrrolidone) (PVP) with poly(vinyl formal) blends. Their results showed that at low PVP concentrations T_g showed a negative deviation from the linear rule. At high PVP contents, T_g showed a positive deviation from linear behaviour. That there exists an inversion point, $\chi = 0$, for such blend systems has been proposed by Kwei et al. [15]. However, according to Eqs. (9) and (13), it is possible that there exists two cases for such blend systems. The first is when $\chi = 0$ and the second is when $\chi^l < 0$, $\chi^g < 0$ and $|\chi^l| = |\chi^g|$.

Lin et al. [15] have discussed the physical meaning of the Kwei equation (Eq. (1)) for the glass transition temperature of polymer blends. The Kwei factor, q, represents the stabilisation energy of the polymer backbone in blend systems which is in excess of the weighted mean of the stabilisation energies of the components. Here, we will discuss further the physical meaning of the Kwei factor.

The glass transition is, of course, associated with the incipient motion of the polymer backbone segments [16,17]. The product kT_g, where k is the Boltzmann constant, is, therefore, the average thermal energy just sufficient to overcome the energy barriers that, below T_g, immobilize the backbone. The term energy barrier includes here both intramolecular flex energy and intermolecular hole energy [16,17]. The term $q\omega_1\omega_2$ shown in Eq. (1) may be the difference between the excess energies in the glassy and liquid states. Excess energy is the difference between the stabilization energy [15] of the backbones in the blend and the weighted mean stabilization energy of the backbones in the homopolymers. The sources of backbone stabilisation are ultimately contacts that are formed in the solid matrix between segments of the main chain and its environment [15]. According to Lin et al. [15], the blend will have homo-contacts between two units of polymer 1, homo-contacts

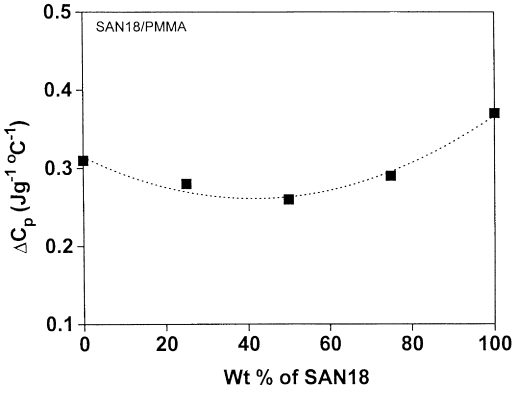

Fig. 7. ΔC_p versus composition for SAN18/PMMA blends.

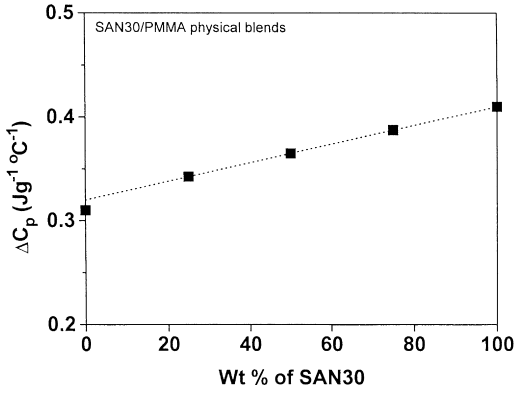

Fig. 9. ΔC_p versus composition for SAN30/PMMA physical blends.

between units of polymer 2, and hetero-contacts between a unit of polymer 1 and a unit of polymer 2. If the volume fractions of such contacts in the blend are indicated by ϕ_{11}, ϕ_{22} and ϕ_{12}, and their contributions to backbone stabilization by E_{11}, E_{22} and E_{12}, the excess energy, Ω, may be written as follows [15].

$$\Omega = \phi_{12}E_{12} + \phi_{11}E_{11} - \phi_{22}E_{22} - 0.5(E_{11} + E_{22}) \qquad (15)$$

For the glassy state, the excess energy may be divided into three specific cases: (i) when it is greater than in the liquid state; (ii) when it is the same as in the liquid state and (iii) when it is smaller than in the liquid state. For case (ii), the backbone stabilization in the liquid state is the same as in the glassy state, i.e., $|\chi^{l}| = |\chi^{g}|$. This will lead to a linear behaviour of the glass transtion temperature. For case (i), the backbone stabilization in the liquid state is higher than in the glassy state. The segment interactions in the glassy state will be different from those in the liquid state, i.e., $|\chi^{l}| > |\chi^{g}|$. This will lead to a higher glass transition temperature in the blend. For case (iii), the backbone stabilization in the liquid state is lower than in the glassy state, i.e., $|\chi^{l}| < |\chi^{g}|$. This will lead to a lower glass transition.

4. Conclusions

Molecular interactions in miscible polymer blends influence the behaviour of glass transition temperature and the increment of heat capacity versus composition. The behaviour of the glass transition temperature and increment of heat capacity versus composition show negative or positive deviations from the linearity. The Ehrenfest model of second-order transitions and the Flory theory can be used to study the glass transition behaviour and increment of heat capacity versus composition in miscible polymer blends. These behaviours can be explained by postulating an idea that the interaction parameter will change at the glass transition temperature. (1) T_g and ΔC_p verses composition will have a positive and a negative deviation of linear behaviour, respectively, when $\chi^{l} < 0$, $\chi^{g} < 0$ and $|\chi^{l}| > |\chi^{g}|$; (2) T_g and ΔC_p will have a negative and a positive deviation, respectively, when $\chi^{l} < 0$, $\chi^{g} < 0$ and $|\chi^{l}| < |\chi^{g}|$; (3) T_g and ΔC_p will both exhibit linear behaviour versus composition when $\chi = 0$ or $\chi^{l} < 0$, $\chi^{g} < 0$ and $|\chi^{l}| = |\chi^{g}|$. This means that the deviations of T_g or ΔC_p versus composition from linear behaviour may be used to determine the interaction parameter.

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