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Poly(2,6-dimethyl-1,4-phenylene oxide)/polystyrene blends: thermodynamic interactions from glass transition data

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Summary

The glass transition temperatures of several blends of poly(2,6-dimethyl-1,4-phenylene oxide) and polystyrene have been measured by DSC, and the T_g-composition data have been described on the basis of a thermodynamic treatment. A negative enthalpy of mixing and a positive entropy of mixing have been found, in agreement with the well known miscibility of the blend. The presence of a singolarity point in the T_g-composition plot has been evidenced and considered at the light of a theoretical treatment recently proposed.

Introduction

A number of more or less theoretical equations has been proposed up to now to describe the composition dependence of the glass transition temperature T_g of miscible polymeric systems (1-12). Many treatments are semiempirical in nature and contain one or more adjustable parameters. The well known, and often quoted, equation proposed in 1978 by Couchman and Karasz (8,11) does not require the use of adjustable parameters, but unfortunately it cannot be applied to polymeric solutions or blends when specific interactions are present (13). Recently several researchers — including some authors of the present work – have proposed theoretical treatments in which the T_g of miscible polymeric systems is described in terms of the Flory interaction parameter χ and/or the excess thermodynamic functions, e.g. enthalpy and entropy of mixing (13-18).

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A characteristic feature of the experimental T_g-composition curves is that a singular point, i.e. a 'cusp' has been reported for some polymeric systems (6,19-23), in which the T_g's of pure components are separated by a large temperature interval. In this regard, the present authors (17) have shown that the peculiarity appears at a characteristic temperature T_o corresponding to the thermodynamic temperature limit below which the liquid state of the component of higher T_g cannot exist (24,25). Equations applicable to the full concentration range and able to describe satisfactorily the singularity point have already been proposed (17). In the present paper these equations are applied to the T_g data, obtained with great care, of a well-known miscible polymer/polymer system, the poly(2,6-dimethyl-1,4-phenylene oxide)/polystyrene or PPO/PS (26-29). It seems worthwhile comparing the excess thermodynamic functions, obtained from the glass transition data, with those derived from the application of a different analysis (30).

Experimental

The poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was an Aldrich commercial product; its number average and weight average molecular weight, as determined by GPC (90°C in o-dichlorobenzene) are 9,900 and 40,200 respectively. The atactic polystyrene (PS) was supplied by Pressure Chemical Company. Its molecular weight is 100,000 (polydispersity index $M_w/M_n=1.06$). Films of PPO/PS blend, covering the whole range of compositions, were prepared by solvent casting. The two components, in the desired proportions, were dissolved in chloroform to produce a 3 wt.-% homogeneous polymer solutions. The films were first air-dried slowly at room temperature, and, in order to remove all traces of solvent, further dried in a vacuum oven at 100°C for two days.

The calorimetric data were obtained via DSC analysis by using a Perkin Elmer DSC 7, driven by a Unix computer. The external block temperature control system was set at -30°C. The instrument was calibrated with high-purity standards (indium, n-octadecane, naphthalene) at 20°C/min. Dry nitrogen was used as purge gas. The sample weight was about 10 mg. Crystallization of PPO is present in PPO-rich blends, so that the following standard procedure was employed: the samples were first heated up to 260°C and kept at this temperature for 2 min. Afterwards the samples were quickly cooled down to 50°C and rerun at 20°C/min. No crystalline phase was evidenced during the second scan and a single glass transition was observed. Excellent reproducibility of the second and subsequent scans were obtained.

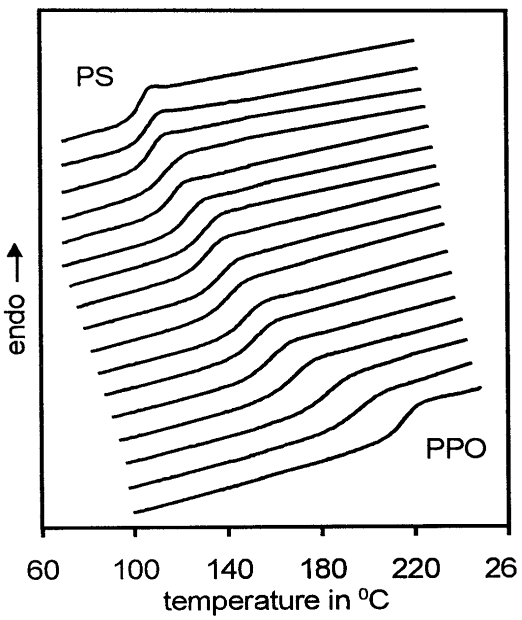

Figure 1 Calorimetric curves of PPO/PS mixtures.

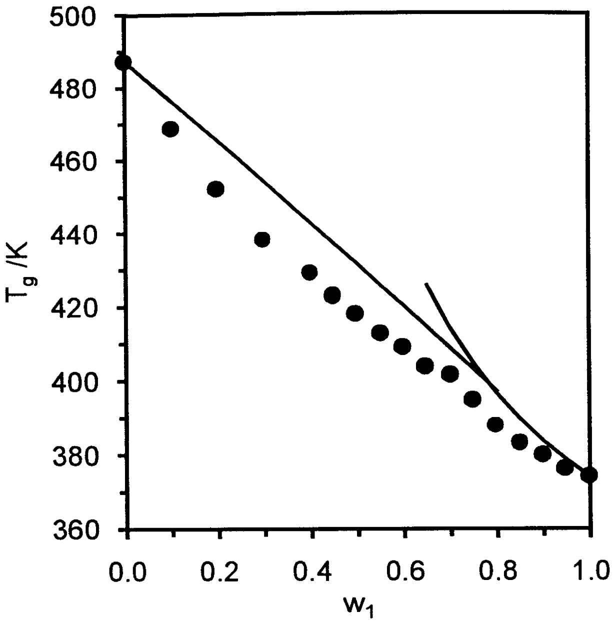

Figure 2 Experimental T_g data for PPO/PS system compared with theoretical curves (see text).

The glass transition temperature T_g was taken as the intersection of the extrapolated pre-transition and post-transition enthalpy data (31) (integration of the calorimetric curves was performed by the Perkin Elmer software package).

Results and discussion

The calorimetric curves of several different composition of the PPO/PS blend are plotted together in Fig. 1 to show the regularity of the data. Each mixture presents only one glass transition, which moves to higher temperatures with increasing PPO content. The corresponding T_g –composition data are shown in Fig.2. A relatively well defined cusp appears at about 400 K. Recently similar T_g data for the PPO/PS blend have been reported (32,33) and evidence of a singular point has been discussed (32). According to our previous work (17), the cusp should be found at a characteristic temperature T_o, below which the liquid state of the component of higher T_g (the PPO) cannot exist, or, in other words, at the PPO 'ideal glass transition temperature' (25), the T_g that could be measured only at an infinitely slow cooling rate.

The temperature dependence of the PPO specific heat increment Δc_p changes at T_o (17); as a consequence two different equations have to be used to describe the T_g –composition curve in the whole composition range. The equations, based either on the entropic or the enthalpic treatment (8,11,17) and on the assumption that the temperature dependence of the pure components Δc_{pi} is of the form:

$$\Delta c_{pi}(T) = \text{costante}/T = \Delta c_{pi}(T_{gi})T_{gi}/T$$

are given here:

for the entropic treatment:

$$T_g > T_o \qquad T_g = \frac{w_1 \Delta c_{p1} T_{g1} + w_2 \Delta c_{p2} T_{g2}}{w_1 \Delta c_{p1} + w_2 \Delta c_{p2} + \left(\Delta s_m{}^l - \Delta s_m{}^g\right)} \tag{1}$$

$$T_g < T_o \qquad \frac{1}{T_g} = \frac{1}{T_{g1}} + \frac{1}{\Delta c_{p1} T_{g1}} \left[\Delta c_{p2} \frac{T_o - T_{g2}}{T_o} + \frac{\left(\Delta s_m{}^l - \Delta s_m{}^g\right)}{w_2} \right] \left(\frac{w_2}{w_1} \right) \tag{2}$$

For the enthalpic treatment:

$$T_g > T_o \qquad \ln T_g = \frac{w_1 \Delta c_{p1} T_{g1} \ln T_{g1} + w_2 \Delta c_{p2} T_{g2} \ln T_{g2} - \left(\Delta h_m{}^l - \Delta h_m{}^g\right)}{w_1 \Delta c_{p1} T_{g1} + w_2 \Delta c_{p2} T_{g2}} \tag{3}$$

$$T_g < T_o \qquad \ln T_g = \ln T_{g1} + \frac{1}{\Delta c_{p1} T_{g1}} \left[\Delta c_{p2} T_{g2} \ln \frac{T_{g2}}{T_o} - \frac{\left(\Delta h_m{}^l - \Delta h_m{}^g\right)}{w_2} \right] \left(\frac{w_2}{w_1} \right) \tag{4}$$

where the w_i's are the pure components weight fractions (1=PS, 2=PPO) and the Δc_{pi}'s the specific heat increments of pure components at the respective T_{gi}. The entropy and enthalpy of mixing in the liquid and in the glassy state (13) are indicated by $\Delta s_m{}^1$, $\Delta h_m{}^1$, $\Delta s_m{}^g$, $\Delta h_m{}^g$.

Fig.2 shows the theoretical curves calculated according to eqs.(1) and (2), with the assumption that the difference ($\Delta s_m{}^1$-$\Delta s_m{}^g$) is zero (T_o = 400 K, Δc_{p1} = 0.27 J g^{-1}K^{-1}, Δc_{p2} = 0.28 Jg^{-1}K^{-1}). Similar curves can be obtained from eqs.(3) and (4) by assuming ($\Delta h_m{}^l$-$\Delta h_m{}^g$)=0. It can be seen that they are far from the experimental T_g data. This can be confidently taken as evidence that intermolecular interactions are present in the system. In this connection a strong interaction between the aromatic rings of the two polymers (28) and between the electron deficient methyl groups in PPO and the phenyl of PS (29) have been suggested.

At the light of the above analysis, the presence of a cusp at about 400 K, shown in Fig. 2, can be easily explained. As a matter of fact, eq.(2) and (4) forecast, for the two function $1/T_g$ and lnT_g respectively, a linear dependence on the compositional ratio w_2/w_1 in the range from w_1=1 to the blend concentration whose T_g is approximately equal to T_o. The plots of Fig.3 and 4 show that the linearity ceases, the data deviating markedly from the

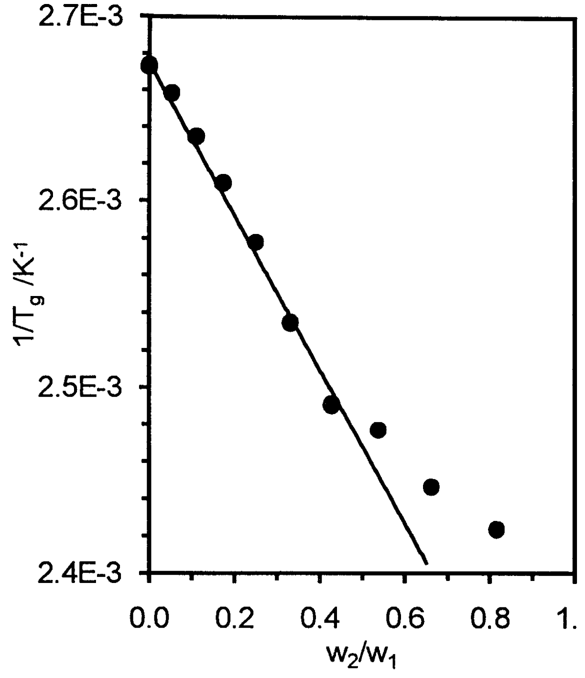

Figure 3 Dependence of $1/T_g$ on w_2/w_1 for PPO/PS mixtures (solid line: linear fit).

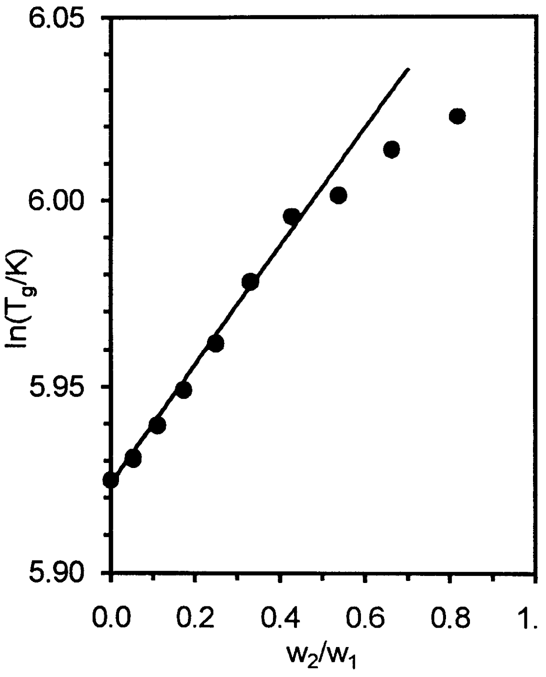

Figure 4 Dependence of lnT_g on w_2/w_1 for PPO/PS mixtures (solid line: linear fit).

straight lines, at w_2/w_1=0.43. Needlees to say, at this ratio T_g is equal to 402 K.

A method that can be used to evaluate an approximate value of T_o has been proposed (17,25). When applied to PPO, it gives for T_o the approximate value of 420 K, not too far from the experimental temperature of the singularity shown in Fig. 2, 3 and 4.

The excess thermodynamic differences (Δh_m^l-Δh_m^g) and (Δs_m^l-Δs_m^g), calculated from the T_g data according to the above eqs. (1)-(4), are plotted in Fig.5 and 6. A relatively well defined maximum is found for both entropy and enthalpy excess differences at about w_1=0.3. At this composition the distance between the calculated curves (Fig.2) and the measured T_g is maximum. It is worth noting that the composition w_1=0.3 corresponds closely to the molar ratio of two PPO repeating units for one PS repeating unit. The singularity of the T_g-composition data, observed in Fig.2 at w_1=0.7, appears to be present, as a not well defined cusp, also in Fig. 5 and 6.

Weeks et al. (30) have also reported data on the excess enthalpy for the PPO/PS blend, obtained by using the Hess thermodynamic cycle, at the constant temperature of 308 K, and in the range of w_1 values going from w_1=0.3 to w_1=0.9. Their data, shown in Fig.5, appear to be in excellent agreement with those of the present work. The mixing of PPO and PS is an exothermal process (30), and it is interesting to point out that for PPO/PS

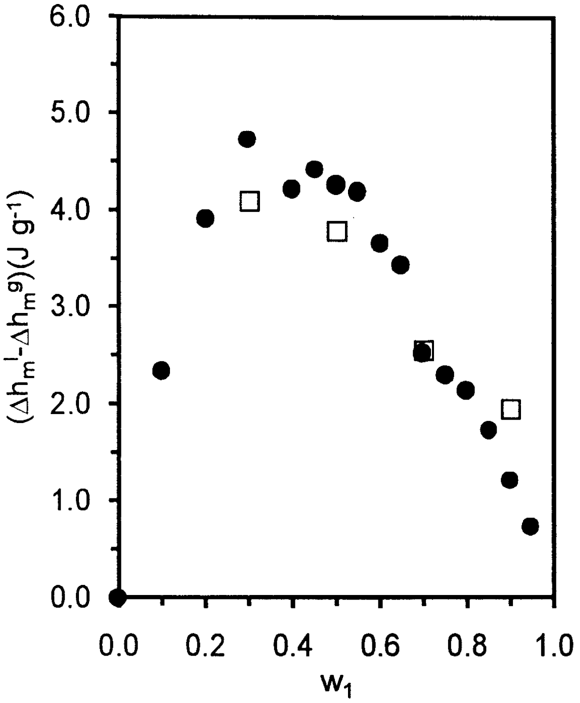

Figure 5 Difference $(\Delta h_m^l - \Delta h_m^g)$ as a function of w_1: (●) calculated at the experimental T_g of PPO/PS mixtures; (□) from ref.(30).

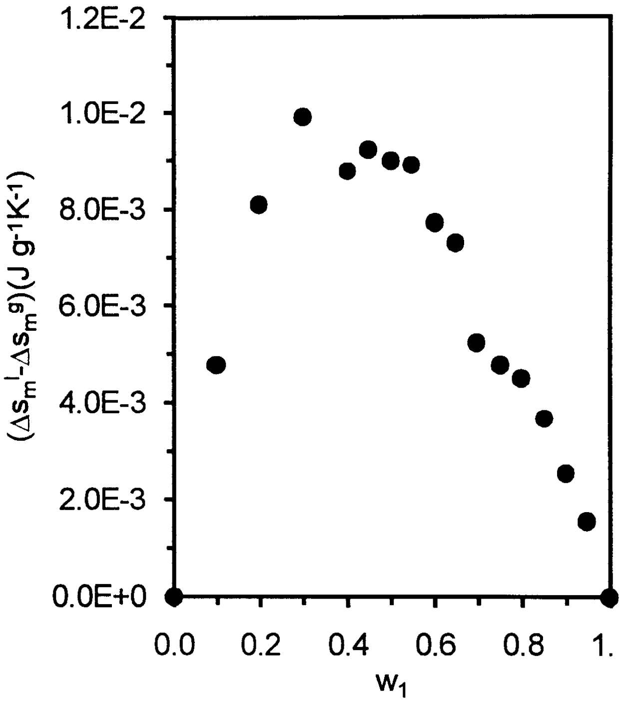

Figure 6 Difference $(\Delta s_m^l - \Delta s_m^g)$ as a function of w_1: (●) calculated at the experimental T_g of PPO/PS mixtures.

blend negative values of the interaction parameter χ, ranging from –0.02 to –0.17, have been reported in the literature (16,27,34,35).

In an attempt to clarify better the physical meaning of the excess enthalpy, in Fig.7a are shown schematically, as a function of temperature, the enthalpy of: (1) the pure components in the liquid and in the glassy states, i.e. h_1^l and h_1^g, h_2^l and h_2^g (lines crossing at T_{g1} and T_{g2} respectively), (2) the system in which interactions are absent, called 'unmixed', i.e. $h_{um}^l = (w_1 h_1^l + w_2 h_2^l)$ and $h_{um}^g = (w_1 h_1^g + w_2 h_2^g)$ (lines crossing at T_c), (3) the mixed system, in which interactions are present, i.e. h_m^l and h_m^g (lines crossing at T_g). It can be observed that, although Δh_m^l and Δh_m^g are negative, their difference is positive, as in effect found from our T_g measurements.

No data on the mixing entropy of the PPO/PS system are available, even if its approximate value can be calculated from the equation (36):

$$\Delta s_m = -\frac{R}{m_{tot}}\left[\left(n_1 \ln \phi_1 + n_2 \ln \phi_2\right) + \frac{V}{v_1}\phi_1 \phi_2 \chi_S\right] = \tag{5}$$

$$= -R\left[\left(\frac{w_1}{M_1}\ln\frac{w_1\rho_2}{w_1\rho_2 + w_2\rho_1} + \frac{w_2}{M_2}\ln\frac{w_2\rho_1}{w_1\rho_2 + w_2\rho_1}\right) + \frac{w_1 w_2 \rho_1 \rho_2}{(w_1\rho_2 + w_2\rho_1)^2}\left(\frac{w_1}{M_1} + \frac{w_2}{M_2}\right)\chi_S\right]$$

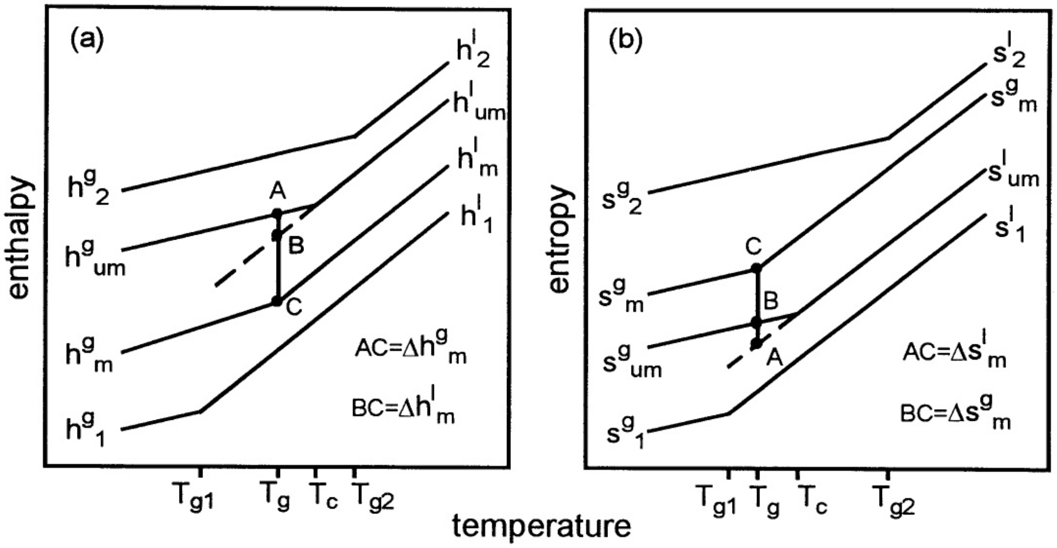

Figure 7 Schematic plot of: (a) enthalpy and (b) entropy as a function of temperature (see text).

where m_{tot} and V are the weight and the volume of the solution, v_1 the molar volume of the polymeric segments and n_i's and ϕ_i's the number of moles and the volume fractions of the components. Moreover ρ_i's indicate the densities of the two polymers and M_i's the molecular weight of the repeating units. χ_S is the entropic component of the interaction parameter χ, as defined by the equation $\chi=\chi_H+\chi_S$. The first term in eq.(5) gives the combinatorial entropy of mixing, the second is related to the interactions.

According to Maconnachie (27), in the temperature range from 380 to 550 K, the value of χ_S is 0.10. When the densities are taken at a convenient average value (w_1=0.45, T_g =423 K, ρ_1^l=0.989 g cm^{-3}, ρ_2^g=1.037 g cm^{-3}) (37), a positive value of the mixing entropy is obtained, since the combinatorial contribute is dominant. In Fig.7b the entropic functions are shown schematically, Δsm^l, Δs_m^g and their difference (Δs_m^l-Δs_m^g) being all positive.

As a conclusion, it can be remarked that the formation of the PPO/PS blend is thermodinamically favoured to a great extent, since negative mixing enthalpy and positive mixing entropy combine.

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