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GLASS TRANSITION TEMPERATURE FOR BLENDS CONTAINING POLY(4-HYDROXYSTYRENE)

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Abstract—The glass transition temperature of poly(4-hydroxystyrene) with poly(vinylacetate), poly(methylmethacrylate) and various poly(acrylates) have been obtained over the whole composition range. The effect of the size of the side-chain group upon the miscibility has been found to be important, leading to partial miscibility for the blends with poly(n-butylacrylate) and poly(methylmethacrylate). On the other hand, the solvent from which the blend is cast has a noticeable effect on the composition dependence of the glass transition temperatures. Finally, the composition dependence of the glass transition temperatures of miscible blends has been correlated in terms of some lattice models.

INTRODUCTION

During the last few years considerable effort has been devoted to the study of polymer blends. This has lead to the introduction of new commercial polymeric materials, whose technological success is achieved either by exploiting the synergistic properties resulting from compatible mixing of the two polymers or by obtaining the desired additive properties. Synergistic properties often result when the components are miscible in the thermodynamic sense, while partially or totally inmiscible blends, most frequently, exhibit intermediate properties with the components [1–4].

Thermodynamic considerations for molecular miscibility of two polymers require that they have a negative free energy of mixing. When two polymers are mixed, no appreciable change in the entropy of the system takes place. The miscibility is solely ascertained by the enthalpy of mixing, which is positive for most polymer pairs. This leads to phase separation of the components and hence the degree of compatibility and the morphology of the polymer blend play an important role in determining their properties [2–4]. Because of this, miscibility of polymer pairs is most often the result of an exothermic heat of mixing; specific interactions are the most obvious source of exothermic mixing, and formation of hydrogen bonds between the two components has shown to be very effective in promoting thermodynamic miscibility [5].

Hydrogen bonding introduces strong difficulties for the theoretical prediction of the thermodynamic properties and the phase diagrams of polymer systems, and even though different authors have addressed this problem in recent papers with encouraging results [6–9], a general predictive calculation of novel polymer mixtures is presently not yet possible, and so experimental studies continue to be of great importance for future work.

The existence of one or several glass transition temperatures (T_g) has been used quite frequently as an indication for thermodynamic compatibility or incompatibility. Technologically, an understanding of the glass transition is important because the mechanical and thermal properties at a polymer blend will strongly depend not only on whether the temperature at which the study is carried out T, is above or below T_g, but also because of $T < T_g$, they will also depend on exactly how the liquid structure is frozen in at the glass transition. The structure of a glass is not unique; it is influenced by the rate at which the equilibrium liquid is cooled into the glassy state, by any subsequent annealing, and by mechanical stresses and strains. Because of this, the T_g is also not unique but is a complex function of the thermal and mechanical history of the sample.

In previous works we have obtained Flory's χ interaction parameters for the poly(4-hydroxystyrene) (P4HS) + Acetone(Ac) [10], polyvinylacetate(PVA) + Ac and P4HS + PVA + Ac [11], using vapour-pressure measurements and the inverse-gas chromatography technique [12]. In addition, Coleman's group has studied the P4HS + PVA [13], P4HS + polyacrylates [14] and P4HS + poly (n-alkylmethacrylates) blends [15] by FT-i.r. spectroscopy, carrying out an evaluation of the hydrogen bonding between the hydroxyl group of P4HS and the carbonyl one of the other polymer.

Besides leading to exothermic mixing, hydrogen-bonding may increase the rigidity of the chains, and therefore have some effects on the glass transition of

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the system [16–20]. Even though there exist many studies on the effect of composition on the location of T_g, [18], we considered it worthwhile to carry out a systematic study for these types of systems. Consequently, in this paper, we will present the T_g results obtained for the P4HS blends with PVA, polymethylmethacrylate (PMMA) and a series of poly(n-alkylacrylates), discussing the effect of the size of the side-chain group upon the miscibility and the effect of the solvent from which the blend is cast. Also, we have tested the ability of some theoretical models to describe the experimental results.

EXPERIMENTAL PROCEDURES

Polymers

P4HS, PVA, poly(methylacrylate) (PMA), poly(ethylacrylate) (PEA), and poly(n-butylacrylate) PBA were purchased from Polysciences (U.K.).

Polymer characterization

The weight-average molecular weight, $M_w = 2 \cdot 10^5$, of PVA was determined at $T = 25°$ by light scattering using a Laser Dawn-F from Wyatt Technology. The incident light was 488 nm and a solution of PVA in acetone with polymer concentration $c < 1.7\ 10^{-3}\,g\,cm^{-3}$ was used. The same polymer solutions measured by light scattering were used to determine $dn/dc = 0.104$ (n is the refractive index). The polydispersity index of this sample of PVA determined with a Waters 510 instrument in tetrahydrofurane (THF) solutions was $M_w/M_n = 2$.

Two samples of P4HS have been used. The number-average molecular weights, $M_n = 5100$ and $M_n = 1500$, were determined at 45° in benzil using a Knauer vapour pressure osmometer. The concentration range spanned was $c < 1.10^{-3}\,g\,cm^{-3}$. The polydispersity index $M_w/M_n = 2$ for both samples was obtained with the same instrument and under the same conditions than above.

It is well known that the hydroxyl groups of P4HS may be oxidized to quinone ones [21]. However, both FTIR and ^1H and ^{13}C-NMR spectra showed that the concentration of quinonic groups was almost negligible.

The viscosity average molecular weights, M_v, for PMA, PEA and PBA were $M_v = 1.1\ 10^5$, $M_v = 6.8\ 10^5$ and $M_v = 8\ 10^4$ respectively. Viscosity has been measured at 25° for PEA and PBA and at 30° for PMA in a modified Ubbelohde viscometer. Polymer solutions in benzene for PMA and PEA and in acetone for PBA, with $c < 0.8\ 10^{-2}\,g\,cm^{-3}$, were used. In order to obtain M_v from the intrisic viscosity, $[\eta]$, Mark–Houwink equations were taken from Ref. [22].

Two samples of monodisperse PMMA were obtained from Polymer Laboratories LTD with $M_w = 8.8\ 10^4$ and $M_w = 1.1\ 10^5$ as determined by light scattering [23].

Solvents

The blends were prepared by solution casting with acetone (Ac) or tetrahydrofurane (THF) as solvents. Ac and THF were Carlo Erba (RPE type).

Differential scanning calorimetry (DSC)

DSC measurements were carried out in a Perkin–Elmer DSC-4 apparatus, over the range −50° to 200°. In all the cases, the heating rate was 20°/min. Open aluminium pans were used with a sample weight ranging from 5 to 10 mg; the measurements were made under a N_2 atmosphere and subambient temperatures were reached using liquid N_2 to cool the DSC cell. The temperature scale has been established using the indium melting-point as reference. The T_g has been taken at the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glassy base lines.

FT-i.r. measurements

The FT-i.r. spectra were obtained using a Galaxy model apparatus from Mattson at a $2\,cm^{-1}$ resolution and in the transmision mode. At least 32 scans were averaged for each spectrum. The films of the blends were cast directly onto KBr windows from solutions of concentrations below 1% in the weight; care was taken to keep the films thin enough for the Lambert–Beer law to be valid. The solvent was eliminated from the films according to the procedure described below.

Preparation of the blends

As already mentioned, the blends were obtained by casting. In the P4HS + PVA system, solutions of P4HS and PVA in Ac or in THF were used; in the other systems only Ac has been used as solvent. The concentration was always below 3% in polymer weight.

The complete elimination of the solvent has to be guaranteed in order to obtain reproducible results. Since this happened to be a non-trivial problem, the procedure followed will be described in some detail. First, the solution was left open to ambient until most of the solvent was evaporated. In a second step, the sample was kept under vacuum and at ambient temperature for five days, and at 60° ten more days. With this procedure, the first DSC scan still showed peaks arising from solvent vaporization. Moreover, the T_g increased in subsequent scans, specially in blends cast from THF, and simultaneously a mass lost was observed.

While for blends cast from Ac constancy both in T_g and in weight was obtained at the third scan. For blends cast from THF, up to nine scans were necessary. For the later systems, keeping the samples in the DSC oven during 30 min, under N_2 atmosphere, and at 50° degrees above T_g lead to the same results as the nine scans referred to above. Therefore, this was the procedure used for the blends cast from THF. It was checked that for the blends cast from Ac this procedure lead also to the same results as the three scans.

Table 1 summarizes the systems that have been studied, as well as the abreviated names that will be used hereafter. The composition will be expressed as weight per cent of the second component.

Table 1. Polymer blends used in this work, and their abbreviated names

Blend	Abreviated name	Solvent for casting
P4HS (5100) + PVA	D1	THF and Ac
P4HS (1500) + PVA	D2	THF and Ac
P4HS (5100) + PMA	D3	Ac
P4HS (5100) + PEA	D4	Ac
P4HS (5100) + PBA	D5	Ac
P4HS (5100) + PMMA*	D6	THF and Ac
P4HS (1500) + PMMA†	D7	THF and Ac

*$M_w = 87.500$.
†$M_w = 105.000$.

Table 2. Values of T_g for the homopolymers

Polymer	Solvent for casting	T_g(K)	Polymer	Solvent for casting	T_g(K)
P4HS (5100)	THF	430	P4HS (1500)	Ac	410
P4HS (5100)	Ac	434	PVAc	THF	315
P4HS (1500)	THF	403	PVAc	Ac	317
PMMA*	THF/Ac	390	PMA	Ac	291
PMMA†	THF/Ac	398	PEA	Ac	262
			PBA	Ac	227

*M_w = 87.500.
†M_w = 105.000.

Table 3. Ratio of free to associated hydroxyls from FT-i.r. data for P4HS with different thermal treatments

Solvent for casting	R M_n = 5100	 M_n = 1500	Thermal treatment
THF	0.27	0.12	None
	0.30	0.33	60 min at 170 and vacuum
Ac	0.22	0.19	None
	0.26	0.32	60 min at 170 and vacuum

RESULTS

Homopolymers

Table 2 shows the T_g values obtained for the homopolymers. As expected, T_g increases with M_w. Only for P4HS has noticeable solvent effect been found, T_g being higher for the P4HS cast from Ac than from THF. Since as already explained, the T_g was measured when no solvent lost was detected, an attractive explanation might be that the different hydrogen bonding capability of each solvent with the hydroxyl groups of P4HS would lead to a different distribution of hydrogen bonds in homopolymer P4HS chains. In order to explain this behaviour FT-i.r. can be used, becasuse as it is known, the hydroxyl stretching band appears in the region 3000–3800 cm^{-1}, (see Fig. 1) and it is formed by a wide band, centred around 3360 cm^{-1}, and a much narrower one centred around 3515 cm^{-1}. The first band is attributed to hydroxyl groups associated by hydrogen bonds according to a wide distribution of hydroxyl groups. The second band is attributed to free or non-associated hydroxyls [24].

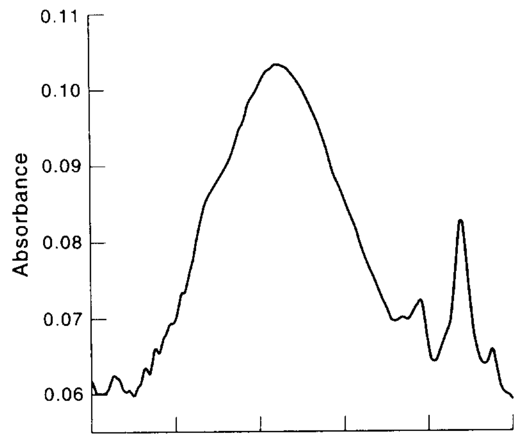

Fig. 1. FT-i.r. spectrum in the region 3800–3000 cm^{-1} recorded at room temperature of P4HS (5100) cast from Ac. Bands at 3515 cm^{-1} and 3360 cm^{-1} correspond to free hydroxyls and hydrogen bonded hydroxyls, respectively.

Table 3 summarizes the results of the FT-i.r. spectra obtained for the P4HS after the same thermal treatment was followed for the DSC experiments. The ratio of the free hydroxyls to that of associated ones, R, was obtained from absorbances corresponding to 3360 cm^{-1} and 3515 cm^{-1}. The results shows that R increases with the thermal treatment, which can be attributed to the breaking of hydrogen bonds between P4HS and the solvent as the later is evaporated. However, after the thermal treatment R does not depend neither on the molecular weight nor on the solvent. Therefore we must conclude that the differences found for the T_gs are not due to differences in the number of hydrogen bonds in the pure P4HS. Nevertheless there might still exist differences in the autoassociative structure in the P4HS chains when cast from Ac or THF.

The system P4HS + PVA

Figure 2 shows the T_g results for the D1 and D2 systems for the whole composition range. As it can be observed, increasing M_w of P4HS leads to a decrease of T_g with respect to the linear interpolation from the T_gs of the pure components. For the D1 system as in the case of homopolymer P4HS, the values of T_g for the blends cast from THF are lower than for those cast from Ac. For the system D2 the differences in T_gs for blends cast from Ac or THF are almost within the experimental uncertainty.

The effect of the molecular weight might be traced back to the structure of the mixture. In effect, a decrease in M_w of P4HS would favour the mixing of both polymers, and hence the formation of hydrogen bonds between the hydroxyl groups of P4HS and the carbonyl ones of PVA. The increase of hydrogen bonds would lead to a higher rigidity of the mixture, and thus to higher T_gs. This explanation is compatible with the FT-i.r. results obtained for blends with $w_1 \simeq 0.5$ and cast from THF. Figure 3 shows the spectra in the 1800–1650 cm^{-1} region characteristic of the carbonyl stretching band. The values of R′ (ratio of free carbonyls to associated ones) were found to be 1.30 for the blend with P4HS (1500) and 1.55 for the

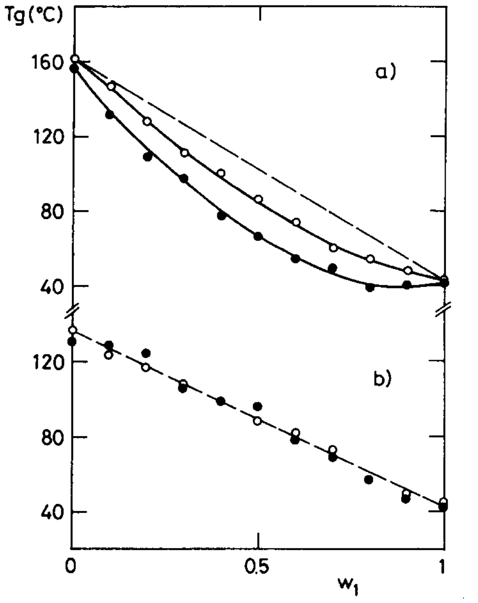

Fig. 2. T_g as a function of weight fraction of PVA in the blend, w_1. (a) System D1; (b) system D2. ○, Ac; ●, THF.

one with P4HS (5100), confirming that the hydrogen bonding is more effective for the blends with P4HS of lower M_w. It has to be pointed out that for the blend with P4HS (5100) cast from Ac, R′ was found to be 1.53, confirming that the solvent has no effect on the number of hydrogen bonds formed in the blend.

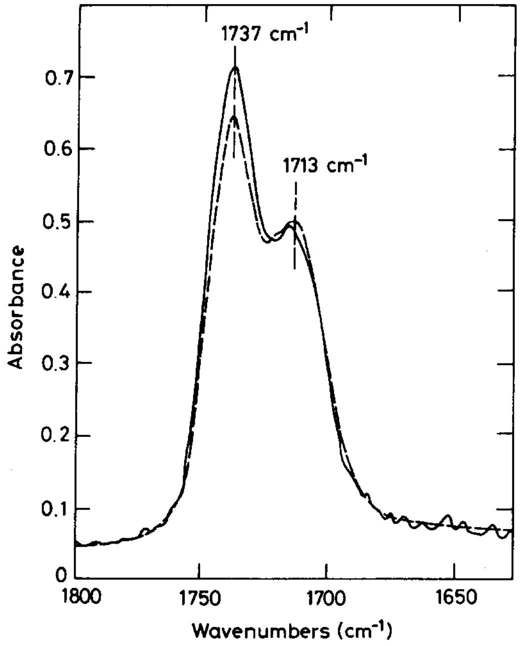

Fig. 3. FT-i.r. spectra in the region characteristic of carbonyl stretching band (——) for system D1 (THF), and (– – –) for system D2 (THF). Bands at 1737 cm^{-1} and 1713 cm^{-1} correspond to free carbonyls and hydrogen bonded carbonyls, respectively.

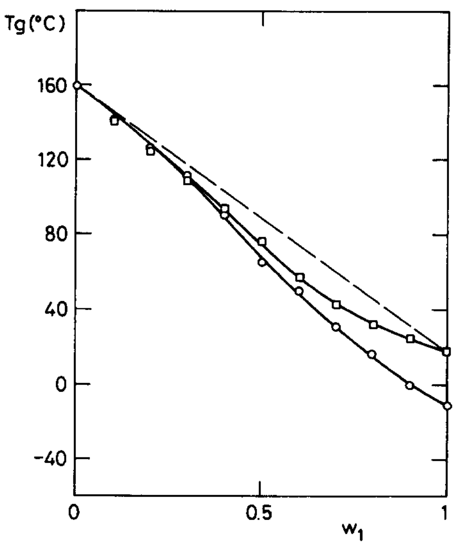

Fig. 4. T_g as a function of weight fraction of polyacrylate in the blend, w_1 system D3(□); system D4 (○).

The systems P4HS + polyacrylates

Figures 4 and 5 show the T_g values over the whole composition range for these systems. It can be observed that the systems D3 and D4 are compatible in the sense that only one T_g is found for each composition. It is possible to compare the behaviour of the D1, D3 and D4 systems since the same P4HS and solvent have been used (Ac). It is clear that for a given w_1 $T_g(\mathrm{D1}) > T_g(\mathrm{D3}) > T_g(\mathrm{D4})$. This is a straight consequence of the decreasing T_g value of the second component $[T_g(\mathrm{PVA}) > T_g(\mathrm{PMA}) > T_g(\mathrm{PEA})]$.

On the other hand, for D1 and D3 systems the departure from the weight-fraction linear interpolation is similar and larger than for D4 system. It might be explained in terms of a more dense hydrogen-bond network in D4 blends.

Using FT-i.r. spectroscopy, Coleman *et al.* [14] have found D1, D3 and D4 systems to be compatible, and a slightly higher fraction of hydrogen-bonded carbonyls for P4HS + PEA than for P4HS + PMA. The behaviour of the D3 and D4 systems is in agreement with the above conclusions.

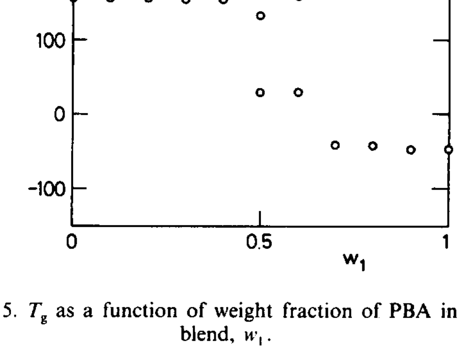

Fig. 5. T_g as a function of weight fraction of PBA in the blend, w_1.

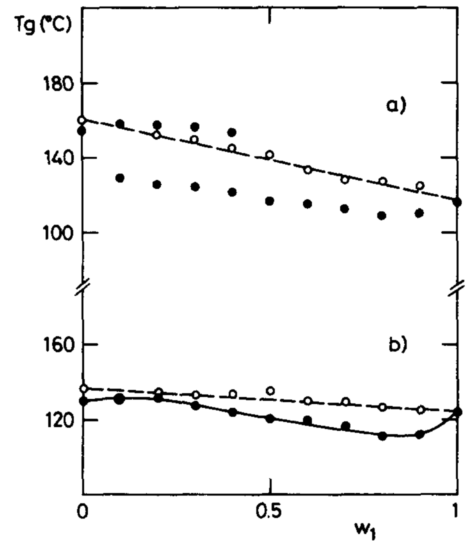

Fig. 6. T_g as a function of weight fraction of PMMA in the blend, w_1. (a) system D6; (b) system D7. ○, Ac; ●, THF.

The results available in the literature for the D5 system are more controversial. In effect, Coleman *et al.* [14] have determined the fraction of hydroxyl groups of P4HS involved in hydrogen bonds with the carbonyl group of PBA. The analogy of their results with those for the D3 and D4 systems lead them to conclude that the D5 systems was "essentially" miscible, even if it might be not far from the phase separation. Calculations with a lattice model suggested that the system is phase-separated at $T < 0°$, then it is miscible over the ranges $0 < w_1 < 1$ and $0 < T < 90$, and finally, for $T > 90°$ and $w_1 < 0.35$ the system re-enters a two-phase region. One of the phases would be almost homopolymer P4HS and the other one a mixture rich in PBA.

Figure 5 clearly shows that the D5 system is inmiscible. In general, the precision of the results for this system is lower than for the previous ones; this makes it difficult to detect the two T_gs in one scan, specially when the T_gs of the pure components are as different as for the P4HS + PBA system. Therefore, where a small amount of the second phase is present it was possible to detect only one T_g, which resulted in an almost equal value to that of pure P4HS for $w_1 \leqslant 0.4$ and similar to that of pure PBA for $w \geqslant 0.7$. For $w_1 = 0.5$–0.6, two phases have been detected, one with high-T_g, that could correspond to pure P4HS and the other one with T_g between the pure component values that could correspond to a mixed phase, which is an evidence of limited miscibility.

The system P4HS + poly(methylmethacrylate)

Figure 6 shows the results for the D6 and D7 systems. As for the D1, the solvent effect is evident in the system D7, while it is more spectacular for the D6 system. In effect, when the blend is cast from Ac, one T_g is obtained for each w_1, but when THF is used as solvent two T_gs are obtained for each mixture in the range $w_1 < 0.5$. This solvent effect is well known in the literature and arises most probably from an inmiscibility window in the polymer-rich region of the P4HS + PMMA + THF system. The high viscosity of the system prevents the miscibility of the two phases once the inmiscibility region has been left out in the solvent-free system. These results are in agreement with those obtained by Takegoshi and Hirichi [25] using ^{13}C/CP/MAS NMR spectroscopy, which indicate that the level of hydrogen-bonds, if any, is so low that is cannot be detected. For the D7 system it is not possible to distinguish from our data whether the inmiscibility window does not exist due to the smaller molecular weight of the P4HS sample, or the smaller difference between the T_gs of the pure components do not allow us to detect two T_gs for those samples.

As it has been pointed out for the P4HS + PVA system, the solvent effect cannot be attributed to hydrogen-bonding differences. Therefore most probably, it is due to differences in the degree of inhomogeneity at a molecular scale of the blends. The term miscibility has to be referred to a microscopic scale in the blend; in effect, the system P4HS + PMMA is found to be compatible with techniques that probe the system at scales > 300 Å [26], but using ^{13}C/MAS-NMR spectroscopy it is found heterogeneous. Unfortunately no solvent or molecular weight effects were studied.

Correlation of T_g with w_i

Even though the glassy state is a non-equilibrium one, the long relaxation time characteristic of the glasses is responsible of the success of equilibrium theories in describing the T_g in terms of a subyacent second-order transition [27, 28, 17–19, 29–33]. Brekner *et al.* [16] have developed an extended Flory–Huggins model that leads to

$$\frac{T_g - T_{g,1}}{T_{g,2} - T_{g,1}} = (1 + K_1)\phi - (K_1 + K_2)\phi^2 + K_2\phi^3 \quad (1)$$

where $T_{g,i}$ refers to component i, and ϕ is a corrected weight fraction of the polymer with the highest T_g, P4HS in our case, and is defined as

$$\phi = Kw_2/(w_1 + Kw_2) \quad (2)$$

where K_1, K_2 and K are constants, arising from the model, that in general are treated as adjustable parameters. According to the model, K_1 is related to the differences between the interaction energies between contact sites in chains of the same kind and those in chains of different species. K_2 reflects the perturbations in the interactions between sites arising from the different molecular environments in which the sites may be. Finally, K is characteristic of the nature of the polymers and, in the simplest case, is related to a ratio of the T_gs of the two pure polymers.

Brekner *et al.* [16] have shown that, after suitable simplifications, equation (1) may lead to the well known equations of Gordon and Taylor [34]

$$T_g = \frac{w_1 T_{g,1} + Kw_2 T_{g,2}}{w_1 + Kw_2} \quad (3)$$

and to that Fox [35]

$$1/T_g = w_1/T_{g,1} + w_2/T_{g,2}. \quad (4)$$

Table 4. Fitting parameters of equations (1) and (3) for different systems

	Equation (3)	Equation (1)		
System	K	K†	K_1	K_2
D_1/Ac	0.56	0.73	−0.61	−0.71
D_1/THF	0.31	0.73	−1.19	−0.63
D_2/Ac	0.88	0.77	0.19	0.11
D_2/THF	1.16	0.78	0.00	−0.89
D_2	0.88*			
D_3	0.72	0.68	−0.36	−0.90
D_4	0.95	0.61	0.19	−0.62
D_6/Ac	1.20	0.89	0.14	−0.33
D_7/Ac	1.45	0.97	0.89	1.11
D_7	1.07*			

*$K = \rho_1 T_{g1}/\rho_2 T_{g2}$ (density data from Ref. [36]).
†$K = T_{g1}/T_{g2}$

Table 4 includes the values of the parameters of equation (1) and (3) that best fit the experimental data. Figures 7 and 8 show the results, including those of equation (4). It can be observed that equation (1) and (3) account correctly for the experimental results. The failure of equation (4) can be understood in terms of the assumptions necessary to derive it, among which it is accepted that there is a random mixing of the polymer segments in the blend.

Despite the free volume additivity hypothesis implicit in equation (3), it is seen that its predictions are quite close to the experimental data for all the systems. Moreover the value of K obtained from the fits is very close to $K = (\rho_1 T_{g1}/\rho_2 T_{g2})$ in the D_2 and D_7 systems for which density data for the pure polymers are available, as shown in Table 4.

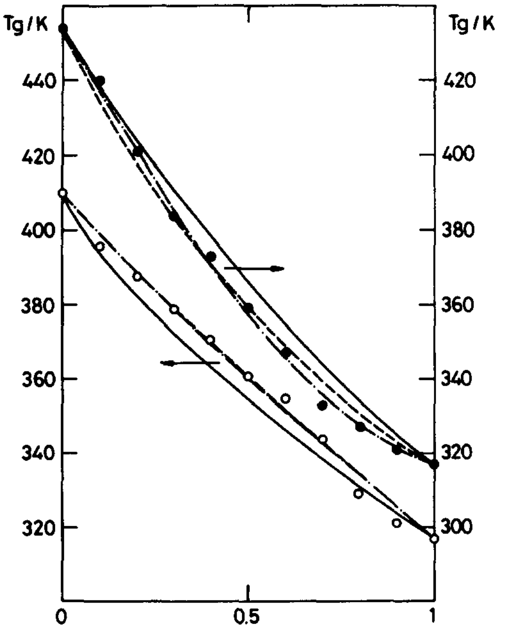

Fig. 7. Composition dependence of the T_g blends of P4HS ●, System D1; ○, System D2. ——, Fox equation; – – –, equation (3); —·—·, equation (1).

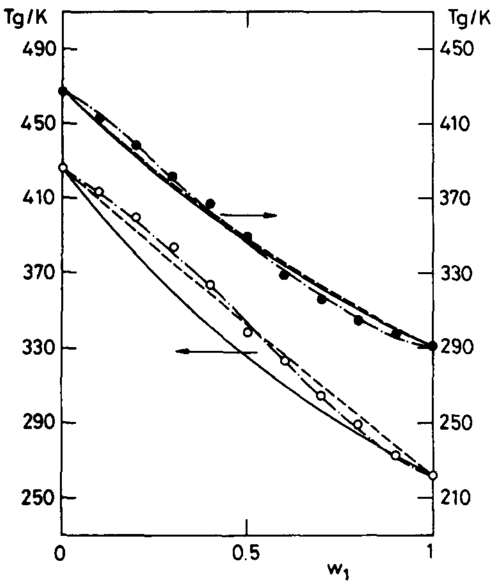

Fig. 8. Composition dependence of T_g blends of P4HS. ●, System D3; ○, System D4. ——, Fox equation; – – –, equation (3); —·—·, equation (1).

For the fits with equation (1), K has been kept constant and equal to the ratio of the T_{gs} of the pure components, in order to diminish the effects of the correlation between the three parameters; with this method the values of K_1 and K_2 are similar to those obtained in the literature for systems with a T_g vs w_1 behaviour similar to those of our systems. The results of Figs. 1 and 3 to 5 indicate that for the present systems the introduction of the two additional parameters K_1 and K_2 do not improve the description of the results.

CONCLUSIONS

The composition dependence of the glass-transition temperature has been measured for blends of containing P4HS plus either PVA, a poly(acrylate) or PMMA. It has been found that the size and nature of the side chain groups have a strong effect upon the miscibility of the system: while P4HS + PMA and P4HS + PEA are fully miscible, only partial miscibility is found for P4HS + PBA. Also the effect of the solvent upon the miscibility of the blend has been found to be important; in effect the P4HS ($M_w = 5100$) + PMMA is found to be compatible (a single T_g for each composition) when cast from acetone, while partial miscibility is found when the blend is cast from tetrahydrofuran. The results are in agreement with FT-i.r. data.

The T_g vs w_1 data have been correlated with a recent lattice model. At least two adjustable parameters are necessary to describe the data of the miscible systems. No cusp-like curves are found even if the differences between the T_gs of the two components is large.

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