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Glass transitions and interactions in polymer blends containing poly(4-hydroxystyrene) brominated

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Abstract

The miscibility and interactions of binary blends of poly(4-hydroxystyrene) brominated (P4HSBR) with poly(ϵ-caprolactone) (PCL), poly(vinyl acetate) (PVA) and poly(vinyl methylether) (PVME) are investigated by means of differential scanning calorimetry (DSC). Glass transition temperatures, T_gs, are used to assess the miscibility of these systems. All of them were found to be miscible over the whole composition range. T_gs of the blends are lower than Fox predictions, in contrast to the results previously obtained for systems involving poly(4-hydroxystyrene) (P4HS). The melting of PCL in the blends was studied. From the melting temperature depression of PCL in the blends the polymer–polymer interaction parameter was obtained and compared with the ones obtained for P4HS/PCL and poly(4-hydroxystyrene-co-methoxystyrene) (P4HSM)/PCL systems. The best interactions are achieved in P4HS/PCL and the bromination or methoxylation of the P4HS worsen the interactions with the PCL. The presence of a cusp in the T_g-composition curve was analysed in terms of the Kovacs' theory in systems with P4HS and P4HSBR.

Keywords: Polymer blend; Glass transition; Interaction

1. Introduction

In previous papers [1–10] we have studied the miscibility of binary blends containing an amorphous polymer poly(4-hydroxystyrene) (P4HS) and a second polymer that had carbonyl or ether groups. The second polymer involves amorphous polymers such as poly(vinyl acetate) (PVA) [1–3,7] polyacrylates, poly(methyl methacrylate) [1,3,4,8], and poly(vinylmethylether) (PVME) [9]or crystalline polymers like poly(ϵ-caprolactone) (PCL) [5,6,10]. The miscibility in these systems was achieved trough hydrogen bond interactions between the hydroxyls of P4HS and the carbonyl or ether groups of the second polymer. The miscibility of binary polymer blends can be assessed by the measurement of a single glass transition temperature, T_g, intermediate between those of pure components. Generally it is observed that T_g shows a monotonic behaviour with composition, that can be explained through several equations [11–14]. Nevertheless a number of polymer blends [15–19] and polymer solvent systems [20–22] have shown a dual dependence of the T_g on composition, with two different curves that lead to a break or cusp at a characteristic temperature, T_c. This T_g behaviour may be theoretically justified on the basis of the free volume theory with the modification suggested by Kovacs' [23,24]. In binary polymer blends the cusp can be observed experimentally when the T_g's values of the two polymers are far apart.

In the case of a crystalline–amorphous polymer pair, the miscibility is confirmed, as in amorphous pairs, through the T_g's of the blends. A single T_g for each blend should correspond to a miscible amorphous phase formed by the amorphous fraction of the crystalline polymer and the amorphous polymer. Furthermore depression in the melting temperature of the crystalline polymer is expected in miscible systems. The melting point depressions can be explained in terms of thermodynamic mixing of a crystalline polymer with an amorphous polymer. From these studies the polymer–polymer interaction parameter can be obtained [26]. The degree of miscibility of the components in the blend is of crucial importance with respect to its morphology and physical properties.

In this work the miscibility of three systems involving poly(4-hydroxystyrene) brominated are studied. The amorphous–crystalline blends: P4HSBR/PCL, and two amorphous systems: P4HSBR/PVME and P4HSBR/PVA. Specifically the T_g's and the melting behaviour are

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determined by differential scanning calorimetry. This offers the chance of make a comparison with analogous systems involving P4HS. In respect of the miscibility, the presence of bromine atoms in the phenol group can have two opposite effects. On one hand the hydroxyl groups become more acidic favouring the hydrogen bonding, on the other hand the big size of bromine gives an steric hindrance for the interactions between polymers.

2. Experimental

2.1. Polymers

All polymers were purchased from Polyscience (UK). PCL, PVA and PVME were the same as were used in previous works [1–10], and their average molecular weight and polydispersity are: for PCL $M_n = 5 \times 10^4$ and $M_w/M_n = 1.6$. For PVA, $M_w = 2 \times 10^5$ and $M_w/M_n = 2$. For PVME $M_n = 9.8 \times 10^4$ and $M_w/M_n = 2$. P4HSBR was obtained from P4HS ($M_n = 1500$ and $M_w/M_n = 2.0$), through a typical reaction of bromination. The brominated polymer contains 50% by weight of bromine, that is an average of 1.5 bromine atoms per each repeating unit.

2.2. PCL blends

Films of PCL, P4HSBR and blends of the two polymers were prepared by mixing appropiate amounts of polymers solutions in tetrahydrofurane (THF) and casting onto a glass surface. Two kinds of samples were used: solution cast samples and melt-crystallized samples.

Solution cast samples were dried under vacuum at 22°C during five days and then scanned in the differential scanning calorimeter.

Melt-crystallized samples were obtained from solution cast samples, that after being dried under vacuum (1 h, 68°C, 5 days at 22°C) were conditioned in the DSC. First, in order to have the polymers in the molten state they were kept at 170°C for ten minutes. Afterwards the samples were fast cooled to the crystallization temperature, crystallized during 45 minutes at 30°C and finally scanned.

2.3. Amorphous blends

P4HSBR/PVA and P4HSBR/PVME blends were prepared in the same way as P4HSBR/PCL blends, using acetone as solvent to get casting films. They were dried under vacuum for 10 h at a temperature about 30°C higher than their glass transition temperature. At least three scans were performed for each sample, second and subsequent scans were identical.

2.4. Differential scanning calorimetry (DSC)

DSC measurements were carried out in a Perkin Elmer DSC4 and a Mettler mod.829 apparatus, both calibrated with Indium. Thermal analysis of the samples was performed at a heating rate of 20° min^{-1} for amorphous blends and 10° min^{-1} for PCL blends, under nitrogen atmosphere in all the cases. Sample weight ranged from 8 to 12 mg. The T_g's were taken at the midpoint of the heat capacity transitions. The melting temperatures of PCL reported were taken at the maximum of the endothermic peaks. The differences of these values with those taken at the endset of the peak are not significant, and both lead to similar thermodynamic results.

Table 1 shows the glass transition temperatures and the melting temperatures determined for the polymers used; also the T_g values of P4HS and poly(4-hydroxystyrene-co-methoxystyrene) (P4HSM) are included.

Table 1
Glass transition and melting temperatures of the polymers

Polymer	T_g (°C)	T_m (°C)
P4HSBR	151	–
P4HS	135	–
P4HSM	100	–
PVME	− 23	–
PVA	42	–
PCL	− 62	58

3. Results and discussion

3.1. PCL blends

3.1.1. Crystallization and melting behaviour of PCL in the blends

The melting behaviour of crystalline polymers depends on the conditions under which they have been crystallized. The thermograms presented in Fig. 1a and b illustrate the behaviour of melt-crystallized P4HBR/PCL samples for several compositions, expressed in weight fraction of PCL, w_{PCL}. Samples of compositions $w_{PCL} \leq 0.5$ present a single T_g. These T_g's are intermediate between those of the pure polymers, suggesting the presence of a unique amorphous phase, that confirms the miscibility of the system. This is consistent with the transparency observed in these amorphous blends. For blends of composition $w_{PCL} > 0.5$ a sharp endotherm corresponding to the melting of PCL appears together with the T_g of the mixed amorphous phase. The crystalline polymer is partitioned between the pure crystalline phase and the mixed amorphous phase.

Fig. 2 illustrates the variation of the glass transition temperatures of the blends with the composition. It can be seen that this variation presents an anomalous behaviour for crystalline blends ($w_{PCL} > 0.5$). This behaviour is corrected when the T_g's are represented vs. the composition of the amorphous phase in the blend. The composition of the amorphous phase in each crystalline blend was calculated using the area of the melting endotherm and the reported value of 32.4 cal g^{-1} for the heat of fusion of 100%

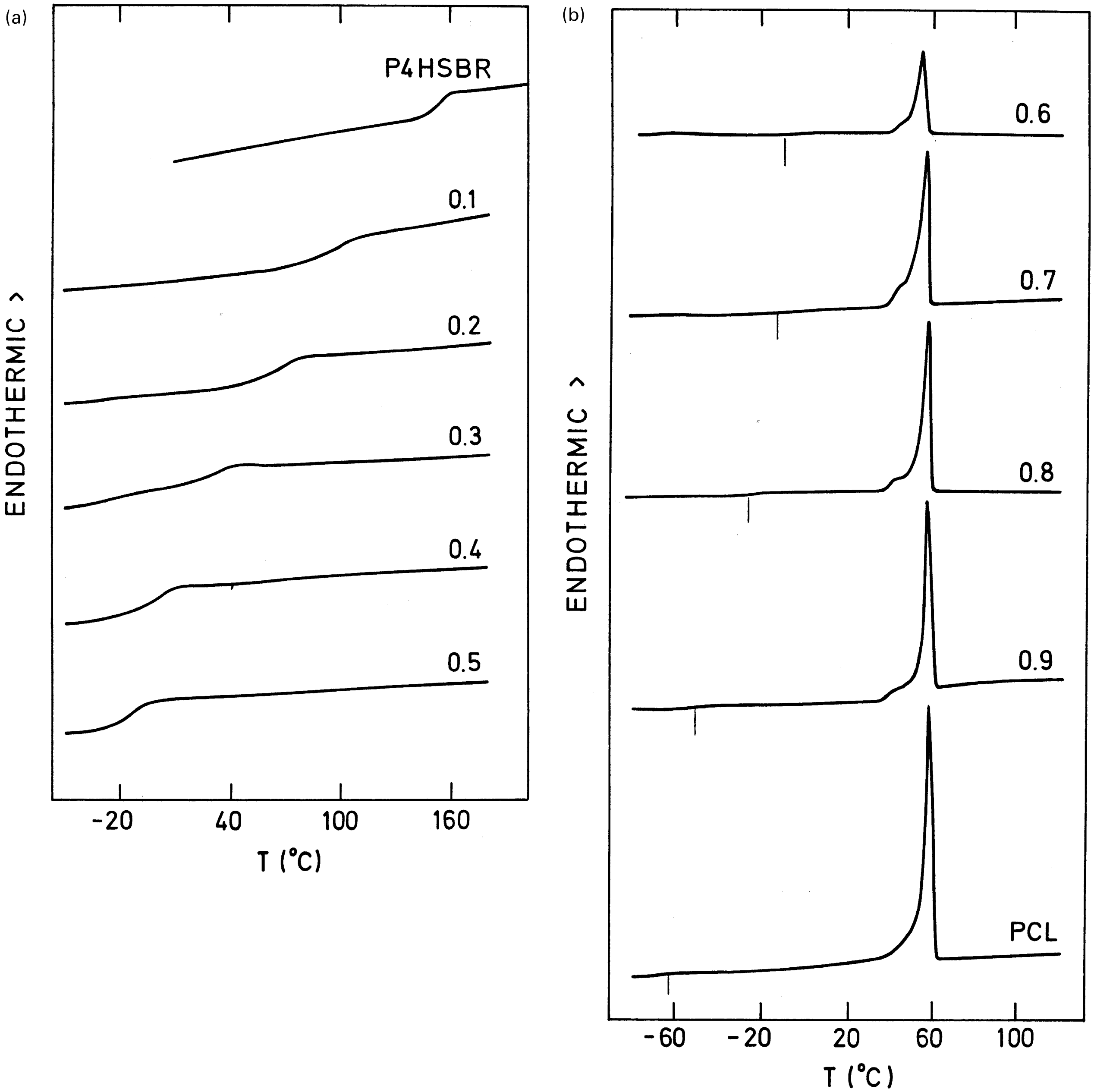

Fig. 1. (a) Thermograms of P4HSBR/PCL blends of composition, $w_{PCL} \leq 0.5$, after isothermal crystallization at 30°C. (b) Thermograms of P4HSBR/PCL blends of composition, $w_{PCL} > 0.5$, after isothermal crystallization at 30°C. The T_g's of the blends are marked on each thermogram.

cystalline PCL [27]. Fig. 2 also shows the dependence of the PCL melting temperature, T_m, on the blend composition. T_m is plotted vs. the overall composition of the blends, because the endotherms peaks (see Fig. 1) correspond to the melting of the polymer crystals that were crystallized from those blends. A melting temperature depression of the PCL in the blends is detected, as a consequence of the miscibility of the system.

The presence of P4HSBR can perturb the crystallization kinetics of PCL upon cooling from the molten state. In Fig. 3 the measured heats of fusion per unit mass of the blend versus w_{PCL} are shown for P4HSBR/PCL, P4HSM/PCL and P4HS/ PCL systems [10,27]. It is apparent that the crystallinity ranges for P4HSBR/PCL and P4HSM/PCL are almost equal ($w_{PCL} = 1$ to ~ 0.55) but it is shorter for P4HS/ PCL system ($w_{PCL} = 1 - 0.70$). The crystallinity depends on the T_g of the blend. The PCL presents a low T_g (−62°C), and the amorphous polymer a much higher T_g (see Table 1), so when the amount of PCL in the blend decreases, the T_g of the blend rises and gives a stiffer matrix that delays the diffusion of PCL and the crystallization becomes inhibited. There is not a correlation of the crystallinity range with the T_g of the amorphous polymer in each system, nevertheless the range of crystallinity seems to be related with the T_g of the blend

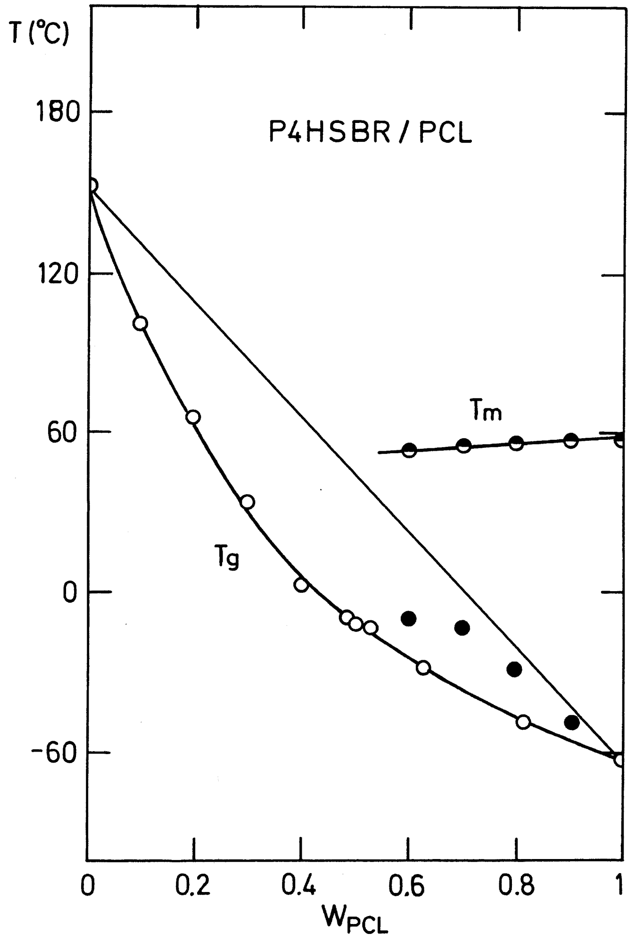

Fig. 2. Plot of the glass transition temperatures, T_g, versus the global blend composition (●) and versus the composition of the amorphous phase in the blend (○) and plot of the PCL melting temperature versus the global blend composition. (◓) for P4HSBR/PCL.

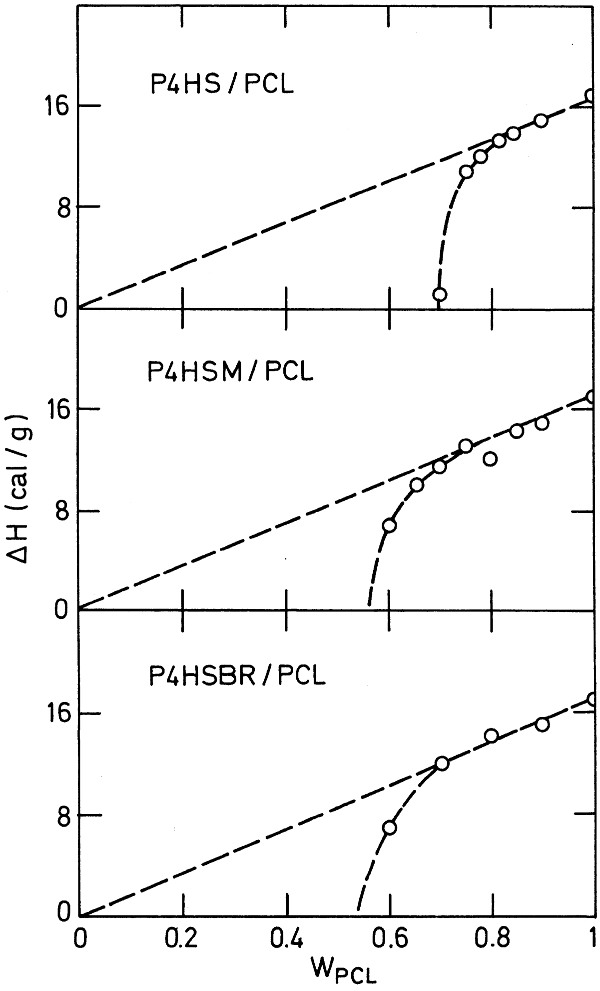

Fig. 3. Heat of fusion per unit mass of the blend sample, versus w_{PCL} for samples of P4HSBR/PCL crystallized at 30°C. The straight line represents the ideal behaviour in which the amorphous polymer does not interfere with PCL crystallization.

from wich the crystallization takes place. For P4HSBR/PCL the crystallinity dissapears at $w_{\mathrm{PCL}} = 0.54$, the corresponding T_g for this composition is −16°C (see Fig. 2). For P4HSM/PCL and P4HS/PCL the crystallinity vanishes at $w_{\mathrm{PCL}} = 0.56$ and $w_{\mathrm{PCL}} = 0.69$, being their respective T_g's −18 and −20°C. As a consequence it can be deduced that PCL only crystallizes from molten blends which have a T_g lower than about −18°C.

The degree of crystallinity of PCL in the blends, was calculated from the heat of fusion of each blend and the heat of fusion of 100% crystalline PCL [26]. In the blends the degree of crystallinity of PCL remains almost constant (~52%) for compositions that follow a linear behaviour in Fig. 3. So for these compositions the kinetic of crystallization of PCL seems to be not perturbed by the other polymer.

For solution cast samples the melting behaviour was similar, but the crystallinity ranges are larger in all the systems, due to the plasticizing action of the solvent, that lowers the T_g's and favours the crystallinity.

3.1.2. Polymer–polymer interaction parameters

The depression of the melting point of the crystalline component of a mixture where the amorphous phase is a miscible blend can be used to obtain the polymer–polymer interaction parameter. Thermodynamics predicts that the chemical potential of the crystallizable polymer is decreased due to the presence of the amorphous component, resulting in a decrease in the melting point. This can be analysed using the equation derived by Nishi and Wang [25] based on the condition that at the melting point the chemical potential of the crystalline component in the crystalline and liquid phases should be identical:

$$\left(\frac{1}{T^0_{\mathrm{m,b}}} - \frac{1}{T^0_{\mathrm{m}}}\right) + A = -\frac{R}{\Delta H_{2\mathrm{u}}}\frac{V_{2\mathrm{u}}}{V_{3\mathrm{u}}}\chi_{32}(1 - \varphi_2)^2 \qquad (1)$$

where $V_{2\mathrm{u}}$ and $V_{3\mathrm{u}}$ are the molar volumes of the repeating unit of the polymers, $\Delta H_{2\mathrm{u}}$ is the heat of fusion per mole of 100% crystalline PCL, φ_2 is the volume fraction of the PCL;

the subscript 2 always refer to PCL and the subscript 3 to the amorphous component, χ_{32} is the polymer–polymer interaction parameter and $T^0_{m,b}$ and T^0_m are the equilibrium melting temperatures of the PCL in the blends and in pure state respectively. The term A represents the entropic contribution and is given by:

$$A = \frac{R}{\Delta H_{2u}} \frac{V_{2u}}{V_{3u}} \left[\ln \frac{\varphi_2^2}{x_2} + \left(\frac{1}{x_2} - \frac{1}{x_3} \right)(1 - \varphi_2) \right] \qquad (2)$$

being x_2 and x_3 the degrees of polymerization.

The experimental melting temperatures determined for PCL (see Fig. 2) can be affected not only by thermodynamic factors, but also by morphological ones such as the lamellar thickness. The morphological contribution to the melting point depression is conveniently eliminated using the Hoffman–Weeks equation [28] to obtain the equilibrium melting temperatures. This equation predicts a linear relation between the temperature of crystallization, T_c, and the observed melting temperature, T_m:

$$T^0_m - T_m = \phi(T^0_m - T_c) \qquad (3)$$

where ϕ is the stability parameter which depends on the crystal thickness. ϕ takes values between 0 and 1, $\phi = 0$ means that crystals are perfectly stable ($T_m = T^0_m$ for all T_c) and $\phi = 1$ reflects inherently unstable crystals. The equilibrium melting temperatures are obtained from the extrapolation of the above equation to $T_m = T_c$. In the system previously studied, P4HS/PCL [5,6] we have found that the melting of PCL obeys the Hoffman–Weeks equation with a stability parameter of, $\phi = 0.18$ in pure state as well as in the blends in which PCL present a high degree of crystallinity. Only for compositions in which the crystallization is very affected by the presence of the amorphous component, $w_{PCL} = 0.7$ (see Fig. 3) the parameter ϕ takes a higher value of 0.24. This means that the crystals of PCL present the same stability independently of the blend composition whenever the amorphous component does not interfere with the crystallization. Accordingly, in P4HSBR/PCL blends, the values of T^0_m have been obtained from the observed melting temperatures at $w_{PCL} \geq 0.6$ (see Fig. 2) using Eq. (3) with $\phi = 0.18$.

In order to obtain the polymer–polymer interaction parameter, χ_{32}, we have applied Eq. (1). The volume fractions, φ_i, were calculated using the data densities: d(P4HSBR) = 1.8 g cm^{-3} and d(PCL) = 1.08 g cm^{-3}. Fig. 4 shows the plot of $(1/T^0_{m,b} - 1/T^0_m + A)$ versus $(1 - \varphi_2)^2$. As expected, a linear correlation was obtained giving an intercept close to zero, and a slope value of 5.09×10^{-4} K^{-1}. Using the data $\Delta H_{2u} = 3690$ cal mol^{-1}, $V_{2u} = 105$ cm^3 mol^{-1} [26,29] and $V_{3u} = 141$ cm^3 mol^{-1} [30], the interaction parameter has been obtained, $\chi_{32} = -1.3$. When the same calculations are made without considering the entropic contribution (A = 0), the interaction parameter obtained results slightly lower ($\chi_{32} = -1.5$). These lower values indicate that the polymer pair presents a good favourable interaction due to the hydrogen bonding between the hydroxyls groups of P4HSBR and the carbonyl groups of PCL.

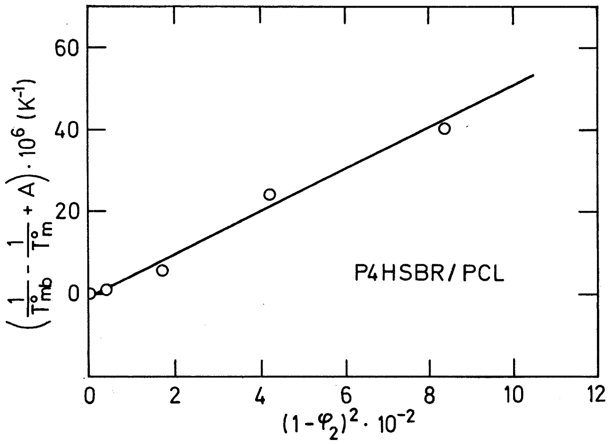

Fig. 4. Plot of $(1/T^0_{m,b} - 1/T^0_m + A)$ versus $(1 - \varphi_2)^2$ for the system P4HSBR/PCL.

The same calculation procedure was applied to the melting data that we have determined previously for P4HSM/PCL [10]. The polymer–polymer interaction parameters obtained for P4HSBR/PCL and P4HSM/PCL, together with the ones we have reported for P4HS/PCL [5,6] are summarised in Table 2. As χ_{32} represents the polymer–polymer interaction parameter referred to the molar volume V_{3u}, the values χ_{32}/V_{3u} were calculated, in order to compare the results obtained in the three systems studied. In all the cases to avoid the entropic contribution gives an interaction parameter about a 20% more negative. The molecular weights of the amorphous polymers are small which leads to a favourable entropic contribution to the mixing that can not be ignored.

The results shown in Table 2 indicate that the most favourable interaction between polymers is obtained for the system involving P4HS, in this polymer all the hydroxyls groups are available to interact through hydrogen bonding with the carbonyls groups of PCL or with themselves. The polymer P4HSM has a 60% of the original hydroxyls groups methoxylated, so they are not available to interact through hydrogen bonding. In the study of FTIR that we have carried out previously [10] it was proved that both polymers in pure state present part of the hydroxyls associated and part of them free. But when they were mixed with PCL (P4HS/PCL and P4HSM/PCL) all the hydroxyls

Table 2
Polymer–polymer interaction parameters obtained from melting temperature depression of PCL

System	χ_{32}/V_{3u} (mol cm^{-3})^a	χ_{32}/V_{3u} (mol cm^{-3})
P4HSBR/PCL	-1.1×10^{-2}	-0.9×10^{-2}
P4HSM/PCL	-1.1×10^{-2}	-1.0×10^{-2}
P4HS/PCL	-1.35×10^{-2}	-1.1×10^{-2}

[a] Without taking into account the entropic contribution.

groups were involved in hydrogen bonds, no detecting free –OH groups. Moreover the presence of PCL decreases the tendency of autoassociation of both polymers. The higher value of χ_{32}/V_{3u} here obtained for P4HSM/PCL than for P4HS/PCL indicates that the methoxylation of the polymer makes less favourable the interaction between polymers. The system involving P4HSBR present the highest value of χ_{32}/V_{3u}, i.e. the worsen interaction with PCL. This can be explained taking into account that in P4HSBR half of the hydroxyls groups are surrounded by two bromine atoms, so it implies a steric hindrance for the hydrogen bonding.

Finally it is worthy to note that when the calculations are made using the experimental melting temperatures instead of the equilibrium melting temperatures the χ_{32}/V_{3u} values obtained are about a 15% higher, however the same conclusions are reached.

3.1.3. Glass transition temperatures

The presence of a unique T_g intermediate between the T_g's of the pure polymers in all the blends studied confirms that the PCL is miscible with the three polymers P4HS, P4HSM and P4HSBR in the whole composition range. However the different interaction of PCL with these polymers influences the T_g-composition behaviour. As can be seen in Fig. 5 each system shows a characteristic T_g–w_2 dependence. The experimental data have been fitted to a third order polynomial. The Fox relation [12] is usually used to describe the T_g dependence of random mixed polymer blends:

$$\frac{1}{T_g} = \frac{\omega_2}{T_{g2}} + \frac{\omega_3}{T_{g3}} \tag{4}$$

where T_{gi} $(i = 2, 3)$ and T_g, refer to the T_g of the pure polymers and of the blend of composition w_i respectively. This relation is considered an 'ideal' volume additivity equation for the T_g of compatible polymer blends. Fig. 5 shows the predictions of Fox rule. The deviation from the Fox predictions can be used to explain the T_g–w_2 behaviour. For miscible blends with strong interactions between components an upward curvature of T_g–w_2 would be expected, i.e. strong positive deviations from Fox rule, reflecting the increase in stiffness due to interactions [31–34]. On the other hand in the systems here studied another effect have to be considered: the destruction of the self association of the polyhydroxystyrene polymers by the PCL [10]. This effect would cause a lowering of the T_g of the blends from the Fox rule. The T_g values obtained are the balance of these two effects.

Consequently the positive Fox rule deviation shown in P4HS/PCL system, in contrast to the negative deviations of P4HSM/PCL and P4HSBR/PCL ones, reflects that the interactions are better in the first system. Moreover the most negative deviation found for P4HSBR/PCL system, indicates that the interactions between P4HSBR and PCL are worsen due to the steric hindrance of the bromine atoms, leading to looser blends. These results are accordance with the values of the polymer–polymer interaction parameters obtained (see Table 2).

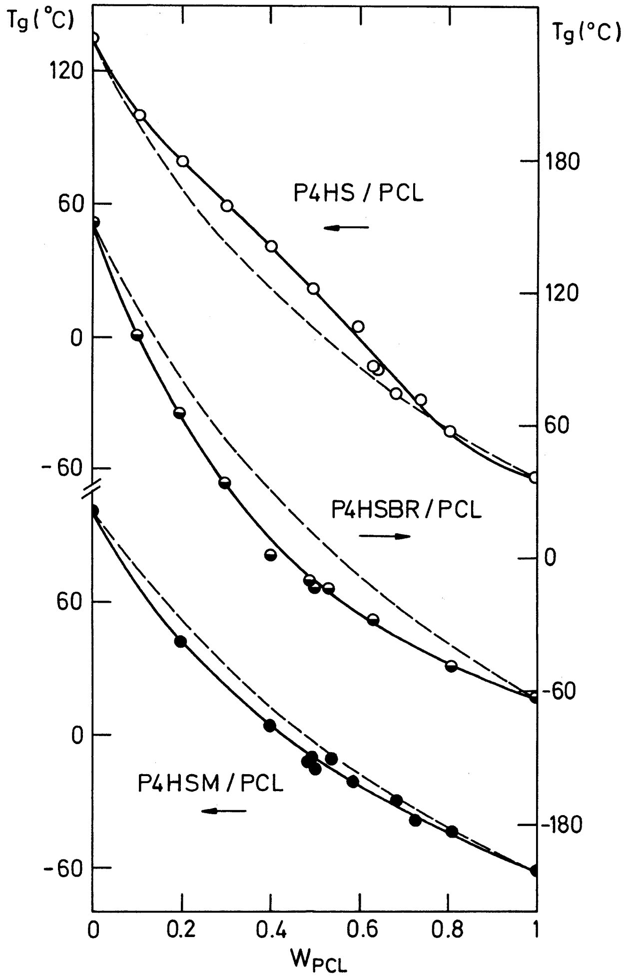

Fig. 5. Plot of the glass transition temperatures, T_g, versus the composition of the amorphous phase in the blend for (a) P4HSBR /PCL (◒) (b) P4HS/PCL (○) (from Refs. [5,6]) (c) P4HSM/PCL (●) (from Ref. [10]). Fitting to a third order polynomial (—) and Fox equation (- - -).

3.2. Amorphous blends

As we have already seen in the crystalline systems the interaction of PCL with P4HSBR is worse than the corresponding with the unmodified polymer, P4HS, giving rise to looser blends. In order to prove the effect of the bromination of P4HS on their blends properties, we have also studied two amorphous systems: P4HSBR/PVA and P4HSBR/PVME. The thermograms obtained for these blends present only a T_g intermediate between those of their respective components, which is taken as a confirmation of miscibility. This is assessed by hydrogen bonding between the hydroxyls groups of P4HSBR and the carbonyls or ethers groups of the second polymer. The T_g's determined covering the entire region of composition are presented in Figs. 6 and 7. The data have been fitted to a third order polynomial. The Fox rule predictions are also shown.

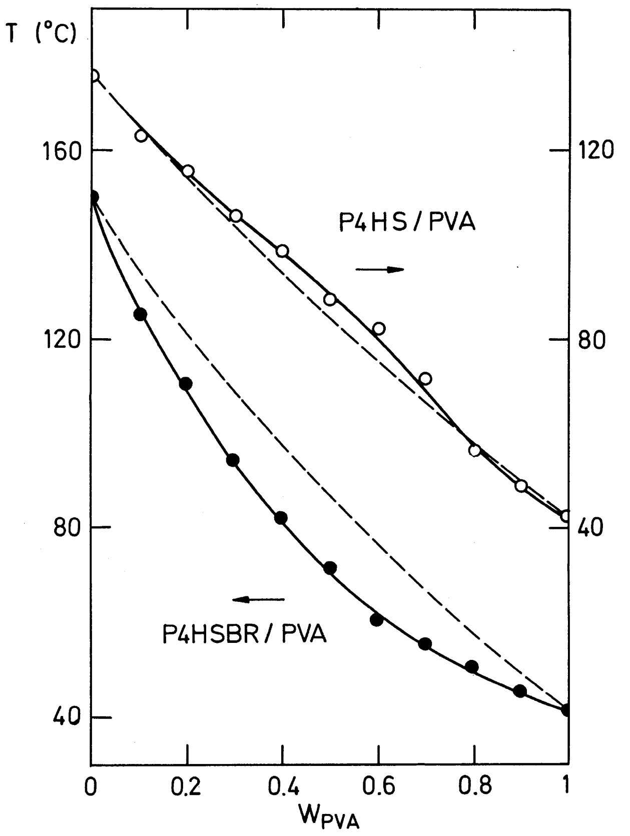

Fig. 6. Plot of the glass transition temperatures, T_g, versus the composition: for the amorphous blends: (a) P4HSBR /PVA (●) and (b) P4HS/PVA (○) (from Ref. [3]). Fitting to a third order polynomial (—) and Fox equation (- - -).

Figs. 6 and 7 also include the results we had previously reported for the systems P4HS/PVA and P4HS/PVME. The comparison of the T_g-composition dependence for P4HS/PVA with P4HSBR/PVA and for P4HS/PVME with P4HSBR/PVME illustrates that the blends involving the brominated polymer present T_g's below the predicted through the Fox rule. However the T_g's of the systems containing P4HS tend to be above the ideal predictions of Fox rule. The results obtained for crystalline and amorphous blends are in agreement, confirming that the systems involving P4HSBR behave less rigid than those with P4HS. Therefore the interactions in blends containing brominated P4HS do not lead to an increase in stiffness because the destruction of the self-association of P4HSBR by the other component causes the opposite effect.

3.3. Analysis T_g-compositon: presence of a cusp

In a first approximation the T_g-composition curves for the blends studied were described fitting a third grade polynomial. However a close view of the plots T_g–w_2 in Figs. 5–7 reveals a non-monotonic behaviour, this effect is emphasised when the T_g's are plotted versus the volume fraction, φ_2, as it is illustrated in Fig. 8a, b and c. The curves appear to be composed of two different lines that meet at a point. In the literature this behaviour has been described as a 'cusp'[15–19]. In practice the cusp appears only in miscible blends when the difference between the T_g values of the two components is higher than about 70°C [16]. This is the case of the systems here studied (see Table 1).

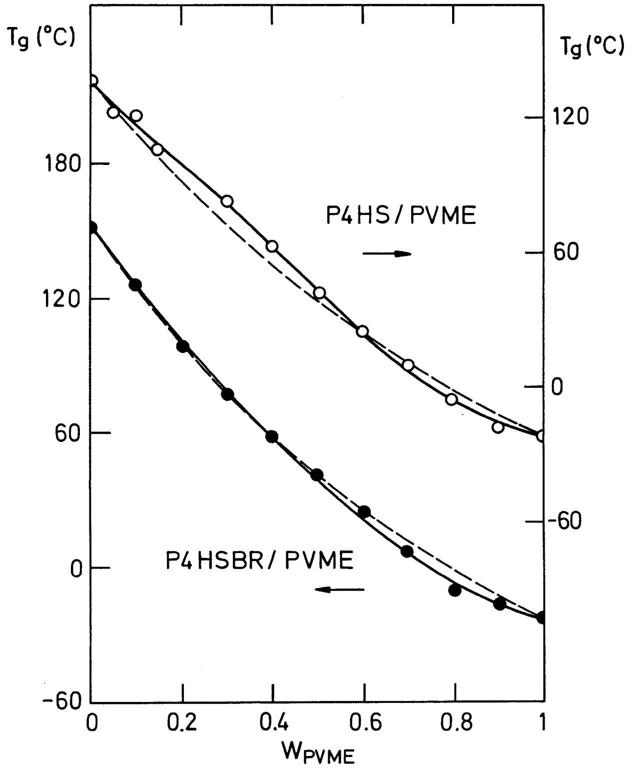

Fig. 7. Plot of the glass transition temperatures, T_g, versus the composition: for the amorphous blends: (a) P4HSBR /PVME (●) and (b) P4HS/PVME (○) (from Ref. [3]). Fitting to a third order polynomial (—) and Fox equation (- - -).

In order to clarify this effect and to compare the behaviour of these systems we have applied Kovacs' theory [23] in the same manner as we do for the data reported for P4HS/PVME [9]. The Kovacs' theory is based on the hypothesis that the fractional free volume of the mixture, f, is given by the weighted sum of the fractioned free volume of pure components, f_i, plus an interaction term:

$$f = \varphi_2 f_2 + \varphi_3 f_3 - g\varphi_2\varphi_3 \tag{5}$$

where φ_i is the volume fraction of the component i and the term, $g\varphi_2\varphi_3$, represents the fraction of excess volume in the mixture:

$$g\varphi_2\varphi_3 = V_e/V \tag{6}$$

In the original theory [24], the excess volume is defined as $V_e = V_2 + V_3 - V$, being, V_2, V_3, V, the volumes of the components (2) and (3) and of the blend respectively. According to this theory if the difference (T_{g3}–T_{g2}) is large, the free volume of polymer 3, becomes zero at a

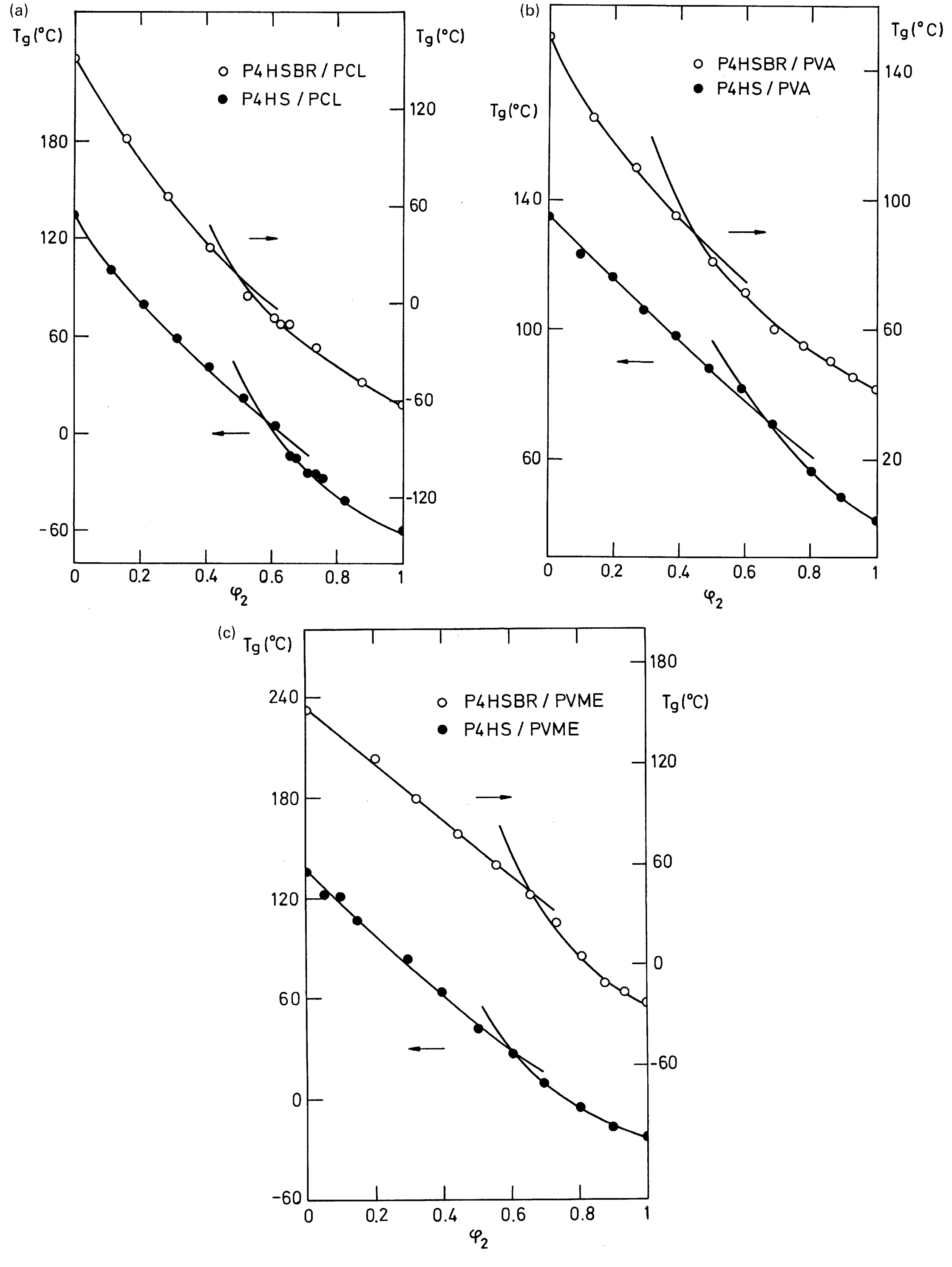

Fig. 8. (a) T_gs of P4HSBR/PCL (○) and P4HS/PCL (●) as a function of the volume fraction of PCL. Kovacs' theory predictions (—). (b) T_gs of P4HSBR/PVA (○) and P4HS/PVA (●) as a function of the volume fraction of PVA. Kovacs' theory predictions (—). (c) T_gs of P4HSBR/PVME (○) and P4HS/PVME (●) as a function of the volume fraction of PVME. Kovacs' theory predictions (- - -).

critical temperature, T_c:

$$T_c = T_{g3} - f_{g3}/\Delta\alpha_3 \tag{7}$$

where the polymer with higher T_g in the blend is denoted with the number 3 and f_{g3} is its fractional free volume at T_{g3}.

The composition dependence of T_g above T_c is given by:

$$T_g = \frac{\varphi_2 T_{g2} + K\varphi_3 T_{g3} + (g/\Delta\alpha_2)\varphi_2\varphi_3}{\varphi_2 + K\varphi_3} \tag{8}$$

being $K = \Delta\alpha_3/\Delta\alpha_2$ and $\Delta\alpha_i$ the difference between the

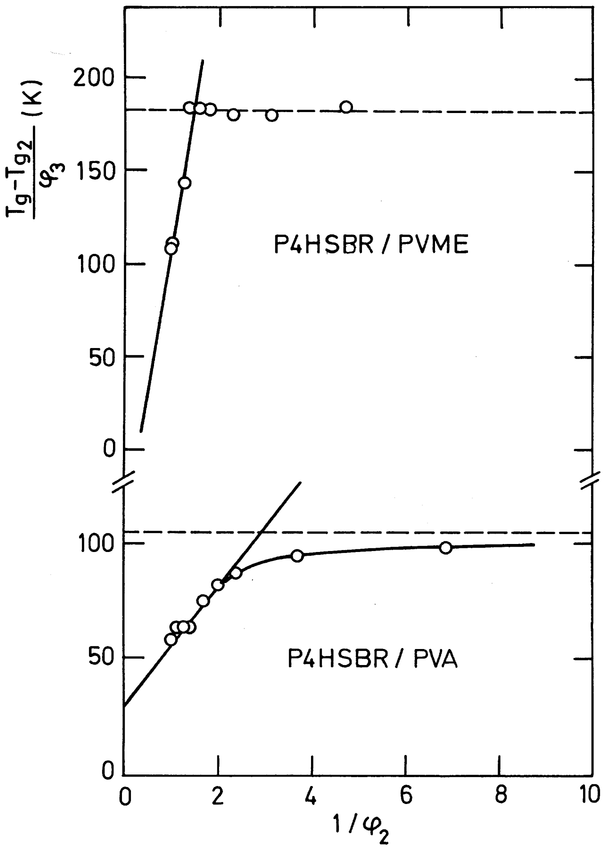

Fig. 9. Plot of $(T_g–T_{g2})/\varphi_3$ versus $1/\varphi_2$ according to Kovacs' theory (—) and the additivity rule (- - -).

volume expansion coefficient in the liquid and glassy states of the *i* component.

When the T_g of the blend is below T_c, T_g is given by:

$$\frac{T_g - T_{g2}}{\varphi_3} = \frac{g}{\Delta\alpha_2} + \left(\frac{f_{g3}}{\Delta\alpha_2}\right)\frac{1}{\varphi_2} \tag{9}$$

On using these equations it has to be noted that the parameters f_{g3}, $\Delta\alpha_2$ and $\Delta\alpha_3$ are somewhat arbitrary, so they have been treated as adjustable parameters. Accordingly to Eq. (9), for $T < T_c$, a plot of $(T_g–T_{g2})/\varphi_3$ versus $1/\varphi_2$ should give a straight line of slope $f_{g3}/\Delta\alpha_2$ and intercept $g/\Delta\alpha_2$. To illustrate it Fig. 9 shows the corresponding plots for the systems P4HSBR/PVA and P4HSBR/PVME. As can be confirmed a straight line describes the behaviour for compositions lower than a critical value, φ_{2c}, which is characteristic of each system. From the least-squares fits of the data the parameters g and $\Delta\alpha_2$ are derived taking $f_{g3} = 0.025$ as usual [35]. Table 3 summarizes the values of these parameters obtained for all the systems here studied. Afterward *K* was calculated using Eq. (8). An almost constant value of *K* was obtained in each system for compositions with a $T_g > T_c$. Then $\Delta\alpha_3$ is obtained as $K\ \Delta\alpha_2$ and the theoretical value of T_c is predicted from Eq. (7). Values of Kovacs' parameters obtained are given in Table 3. Fig. 8a–c show the prediction of Kovacs' theory (Eqs. (8) and (9)) using parameters from Table 3.

Negative values of the Kovacs' g parameter reflect an increase in the free volume in the polymer mixture. So the lower g values obtained for the systems involving P4HS in comparison with those obtained for systems involving P4HSBR, should indicate that P4HS blends are more expanded than P4HSBR ones. However a previous study for P4HS/PVME system [19] has proved that the experimental excess volumes of mixing and Kovacs' predictions are not in accordance. So the g parameter has to be consider as an adjustable parameter. The values obtained for $\Delta\alpha_i$ are in the usual range found for most polymers [36], although no a unique value has been obtained for each polymer, since they have been treated also as adjustable parameters.

The values of T_c obtained (see Table 3) were certainly unexpected, i.e. according to Eq. (7), T_c depends only on characteristics of the polymer of higher T_g, so a unique value should be get for P4HS and also for P4HSBR, irrespective of the polymer with which it is blended. The T_c's here obtained are dependent on the system. Looking for similar cases reported in the literature, some polymer–plasticizer systems with the same behaviour have been found [20,21]. From the data supplied on Table 3 it could be deduced that the variation of T_c is associated with the variation of $\Delta\alpha_3$. Therefore the main reason why the application of Kovacs' theory, to our systems fails, could be the assumption of a unique value of $\Delta\alpha_3$, irrespective of the surrounding media of the polymer. Trying to analyse the variation of T_c, and the influence of the second polymer on it, we have found a correlation between $(T_{g3}–T_c)$ and $(T_{g3}–T_{g2})$ for P4HS and P4HSBR systems (see Table 4). So as larger is the difference $(T_{g3}–T_{g2})$, the polymer with lower T_g brings more free volume to the blend, and the high- T_g polymer reaches the zero free volume at lower temperatures.

Table 3
Parameters of Kovacs' theory

System	g	$\Delta\alpha_2$ ($\times 10^4$ K^{-1})	$\Delta\alpha_3$ ($\times 10^4$ K^{-1})	φ_{2c}	T_c (°C)
P4HS(3)/PVA(2)	−0.01	3	3.8	0.68	71
P4HSBR(3)/PVA(2)	0.03	9.8	4.2	0.46	87
P4HS(3)/PVME (2)	−0.02	1.8	2.2	0.62	25
P4HSBR(3)/PVME(2)	−0.01	1.3	2.3	0.66	43
P4HS(3)/PCL(2)	−0.01	2.1	2	0.58	2
P4HSBR(3)/PCL(2)	0.02	4.3	1.8	0.51	14

Table 4
Differences between the T_g of polymers and T_c

System	T_{g3}–T_{g2} (°C)	T_{g3}–T_c (°C)	φ_{2c}
P4HS(3)/PVA(2)	93	64	0.68
P4HS(3)/PVME (2)	158	110	0.62
P4HS(3)/PCL(2)	197	133	0.58
P4HSBR(3)/PVA(2)	109	64	0.46
P4HSBR(3)/PVME(2)	174	108	0.66
P4HSBR(3)/PCL(2)	213	137	0.51

The ϕ_{2c} values are also dependent on the system (see Table 3). According to Kovacs' theory [16] the critical concentration is sensitive to the (T_{g3}–T_{g2}) difference. The larger this difference is, the closer φ_{2c} appears to the polymer with lower T_g. The systems here studied follow this behaviour with the exception of P4HSBR/PVA. In this system the fitting procedure gives a low value of φ_{2c}, nevertheless experimental results (see Fig. 8) show that the cusp could be located in a certain range. Systems involving P4HS have (T_{g3}–T_{g2}) values lower than the corresponding ones to P4HSBR systems; so the appearance of the break in the T_g-composition curve is located to smaller concentrations.

4. Conclusions

The miscibility of the systems: P4HSBR/PCL, P4HSBR/PVA and P4HSBR/PVME have been studied trough DSC technique. A unique T_g value was obtained for each blend composition, concluding that all the systems were miscible across the whole composition range. The T_g behaviours were compared with those obtained previously for P4HS/PCL, P4HS/PVA and P4HS/PVME systems. The systems involving P4HSBR present T_g values lower than those predicted from Fox's rule while P4HS systems show the opposite behaviour. These T_g results indicate the formation of well bonded rigid structures when P4HS is implicated. From the melting temperature depression of PCL in the blends the polymer–polymer interaction parameter was obtained and compared with the ones obtained for P4HS/PCL and P4HSM/PCL. The main conclusion reached from these studies was that the best interactions are in P4HS/PCL and that the bromination or methoxylation of the P4HS worsen the interactions with the PCL. The presence of a cusp in the T_g-composition curve was analysed in terms of the Kovacs' theory in systems with P4HS and P4HSBR.

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