Glass transition behaviour and interactions in poly(*p*-vinyl phenol)/polymethacrylate blends

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The glass transition temperatures (T_gs) of binary blends of poly(*p*-vinyl phenol) with poly(methyl methacrylate), poly(ethyl methacrylate) and poly(ethyl methacrylate-*co*-methyl methacrylate) have been determined. The experimental T_g–composition data do not obey the Couchman–Karasz equation. However, the Gordon–Taylor, the Kwei and the Schneider equations fit the experimental data quite well. The values of the Gordon–Taylor k parameters, as well as the measurements of the glass transition widths, suggest a similar average intensity of the specific intermolecular interactions in the systems studied here, which is in agreement with the Fourier transform infra-red results. The Kwei and the Schneider equations are able to reflect the additional stabilization due to the dilution of copolymer repulsive interactions in the poly(*p*-vinyl phenol)/poly(ethyl methacrylate-*co*-methyl methacrylate) blends.

(Keywords: blends; miscibility; glass transition temperature; poly(*p*-vinyl phenol); polymethacrylates)

INTRODUCTION

The phase behaviour of polymer blends is governed by several factors: the blending process, molecular weights of the blend components, the specific polymer–polymer interactions and the so-called free-volume effects. Miscible blends are homogeneous at the polymer segment scale, with negative free energy of mixing and are stable against phase separation at constant temperature. The entropic contribution to the Flory–Huggins free energy of mixing is quite small for high-molecular weight polymers and miscibility is often attributed to an exothermic enthalpic contribution[1]. It has been shown that strong specific interactions such as hydrogen bonding[2,3] as well as the dilution of repulsive interactions by less unfavourable ones in blends involving random copolymers[4–6], can produce negative (exothermic) heats of mixing. Thus, an enhanced miscibility for blends will be expected, with both intermolecular specific interactions and the so-called copolymer intramolecular repulsion[7].

A simple and useful method to analyse the miscibility of polymer blends, is the determination of their glass transition temperatures (T_gs) as a function of composition. It has been shown that a single-phase, homogeneous blend will have only one glass transition while a multiphase, partially miscible or immiscible blend will exhibit two transitions. In the literature, T_g–composition data of miscible blends are generally expressed with equations that predict a monotonic variation of T_g. Any deviation of the results from linear behaviour is then considered as a measure of the strength of the interactions involved[8,9]. Some of these equations try to obtain information about the different factors that have an influence on blend miscibility.

In this paper, T_g–composition behaviour of the poly(*p*-vinyl phenol) (PVPh)/poly(ethyl methacrylate-*co*-methyl methacrylate) (EMA-*co*-MMA) system has been analysed by means of different equations. This system offers a way to check the ability of the equations to reflect the different driving forces for miscibility. It is well known that strong specific interactions are involved between PVPh and polymethacrylates through hydrogen bonding[2,10]. The unfavourable interactions between poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) have been previously reported in the literature[11]. Hence, two kinds of factors promoting miscibility are expected for the PVPh/EMA-*co*-MMA system. The first should be the presence of specific interactions, and the second, the dilution of repulsive interactions in the copolymer upon mixing. Consequently, the glass transition analysis of PVPh/PMMA and PVPh/PEMA blends must be done first, in order to judge the influence of the copolymer repulsion effect on blend miscibility. However, since the two mentioned factors are quite possibly orders of magnitude different and the former will be the main factor, the copolymer effect may or may not be visible in this blend system.

BACKGROUND

Over the years, numerous equations have been proposed in the literature to correlate the dependence between the T_g of a miscible blend and its composition. These equations have usually been derived from the so-called free volume hypothesis or from thermodynamic arguments, although several are undoubtedly empirical

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expressions. Generally, they involve one or more of the characteristic adjustable parameters that have a theoretical or empirical meaning such that information about the extent of blend interactions might be extracted from them.

The most important features of the equations used in this paper and their parameters are summarized below. The criterion adopted in the following equations is to denote the polymer in the blend with the higher T_g value as component 2.

Predictive equations

The more general predictive equation is due to Couchman and Karasz and becomes, for a binary blend assuming that ΔC_{pi} does not depend on temperature:

$$\ln T_g = \frac{\omega_1 \Delta C_{p1} \ln T_{g1} + \omega_2 \Delta C_{p2} \ln T_{g2}}{\omega_1 \Delta C_{p1} + \omega_2 \Delta C_{p2}} \tag{1}$$

where T_g is the glass transition temperature of the blend, ω_i is the weight fraction of component i and ΔC_{pi} is the difference in specific heat between the liquid and glassy states at T_{gi}.

This equation was derived from thermodynamic arguments assuming the continuity of the entropy of the mixtures at T_g and requires only the knowledge of pure component properties (like ΔC_{pi} or T_{gi}) to predict the glass transition behaviour of the blend. Furthermore, it can be reduced to several other equations following a certain number of simplifying assumptions[12,13] as shown in *Table 1*.

Single-parameter fitting equations

The most commonly employed equation is the Gordon–Taylor expression[16] with the k parameter treated as an arbitrary fitting parameter:

$$T_g = \frac{\omega_1 T_{g1} + k\omega_2 T_{g2}}{\omega_1 + k\omega_2} \tag{2}$$

The linearized logarithmic version is:

$$\log\left(\frac{T_g - T_{g1}}{T_{g2} - T_g}\right) = \log k + \log\left(\frac{\omega_2}{\omega_1}\right) \tag{3}$$

Using this form a straightforward check on the applicability of the Gordon–Taylor equation can be made: the plot of $\log[(T_g - T_{g1})/(T_{g2} - T_g)]$ *versus* $\log(\omega_2/\omega_1)$ must give a straight line with a slope of 1, and from the intercept, k should be obtained.

The k parameter is often related to the strength of intermolecular interactions between the blend components[8,9]. Positive deviations of linear behaviour ($k = 1$) with the resultant high k values are expected for blends with restricted chain mobility. The Gordon–Taylor expression can be also derived from several theories in which k is no longer an adjustable parameter. The physical meaning then assigned is shown in *Table 2*.

Table 1 Expressions derived from the Couchman–Karasz equation

Assumption	Equation	Name
$k = \Delta C_{p2}/\Delta C_{p1}$	$\ln T_g = \frac{\omega_1 \ln T_{g1} + k\omega_2 \ln T_{g2}}{\omega_1 + k\omega_2}$	Utracki[14]
$\Delta C_{p1} \approx \Delta C_{p2}$	$\ln T_g = \omega_1 \ln T_{g1} + \omega_2 \ln T_{g2}$	Pochan *et al.*[15]
$k = \Delta C_{p2}/\Delta C_{p1}$ Log. expansion $T_{g2}/T_{g1} \approx 1$	$T_g = \frac{\omega_1 T_{g1} + k\omega_2 T_{g2}}{\omega_1 + k\omega_2}$	Gordon–Taylor[16]
$\Delta C_{p1} \approx \Delta C_{p2}$	$T_g = \omega_1 T_{g1} + \omega_2 T_{g2}$	Additivity rule
Log. expansion $\Delta C_{p1} \approx \Delta C_{p2}$	$\frac{1}{T_g} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}}$	Fox[17]

Table 2 Physical meaning of the k parameter in the Gordon–Taylor equation using several derivations[a]

Theory	k
Thermodynamic theory of Couchman–Karasz[12]	$\Delta C_{p2}/\Delta C_{p1}$
Thermodynamic theory of Gibbs–Di Marzio[18]	$\gamma_2 m_1/\gamma_1 m_2$
Volume additivity[19]	$\rho_1 \Delta\alpha_2/\rho_2 \Delta\alpha_1$

[a] ΔC_{pi} is the heat capacity change of polymer i at T_{gi}, γ_i is the number of flexible bonds per monomer unit i, m_i is the molecular weight of monomer i, ρ_i is the density of component i at T_{gi} and $\Delta\alpha_i$ is the expansion coefficient of polymer i at T_{gi}

Two-parameter fitting equations

Generally, these are employed when single-parameter equations fail to describe the experimental T_g–composition data. Two important equations try to relate glass transition behaviour and interactions by means of two adjustable parameters. The first one is the Kwei equation[20]:

$$T_g = \frac{\omega_1 T_{g1} + k\omega_2 T_{g2}}{\omega_1 + k\omega_2} + q\omega_1\omega_2 \tag{4}$$

The $q\omega_1\omega_2$ term was introduced into the Gordon–Taylor equation by Kwei to account for strong specific interactions in the mixture. Recently, a study[21] of blends with electron donor–acceptor interactions has led to the clarification of the physical meaning of the characteristic constant q. In the class of systems where $k = 1$, equation (4) can be written in the form:

$$T_g = (\omega_1 T_{g1} + \omega_2 T_{g2}) + q\omega_1\omega_2 \tag{5}$$

Following Lin *et al.*[21], the parameter q represents the excess backbone stabilization energy in the mixture over the weighted mean stabilization in the pure components. If that excess energy is positive ($q > 0$) it will lead to a higher T_g in the blend whereas negative excess energy ($q < 0$) will lead to a lower T_g than the mean T_g of the components. This excess stabilization energy is small, when compared with the overall stabilization energy of the mixture even though large q values are considered.

If k is not equal to one ($k \neq 1$) but $q = 0$, the Kwei equation reduces to the Gordon-Taylor expression. Several interpretations suggested for the constant k in this equation are shown in *Table 2*.

The second two-parameter equation has been recently developed by Schneider *et al.*[9,19,22] relying on the idea that, besides conformational barriers, contacts due to interactions between the components of the blend are responsible for both conformational and 'free' volume distribution. This theoretical approach employs the concepts of polymer solution thermodynamics and accounts for both chain-specific and interaction-specific contributions. The result is a third-power equation with respect to the concentration of the more rigid polymer component

$$\frac{(T_g - T_{g1})}{(T_{g2} - T_{g1})} = (1 + K_1)\omega_{2C} - (K_1 + K_2)\omega_{2C}^2 + K_2\omega_{2C}^3 \tag{6}$$

where $\omega_{2C} = k\omega_2/(\omega_1 + k\omega_2)$ represents the corrected weight fraction of component 2 supposing volume additivity for the blend components. Thus, the significance of the constant k is given by the expression (see *Table 2*):

$$k=\frac{\rho_1\Delta\alpha_2}{\rho_2\Delta\alpha_1} \qquad (7)$$

Or, assuming the validity of the Simha–Boyer rule[23] ($\Delta\alpha T_g$ = constant), and taking into account the very similar densities of most polymers, k is given by:

$$k=\frac{T_{g1}}{T_{g2}} \qquad (8)$$

The Schneider equation introduces two fitting parameters, K_1 and K_2, which are essentially related to the intensity of the polymer–polymer interaction and configurational redistribution due to orientation effects in the neighbourhood of the binary contacts, respectively[24,25]. Schneider suggests that the larger the values of the fitting parameters, then the larger the interaction.

Equation (6) can be reformulated in the following manner:

$$\frac{(T_g-T_{g1})}{\omega_{2C}(T_{g2}-T_{g1})}=(1+K_1)-(K_1+K_2)\omega_{2C}+K_2\omega_{2C}^2 \qquad (9)$$

Thus, for volume additivity both $K_1=0$ and $K_2=0$, and horizontal straight lines along unity are the result of a plot of $(T_g-T_{g1})/\omega_{2C}(T_{g2}-T_{g1})$ *versus* ω_{2C}. Straight lines of slope K_1 or curved lines are obtained when $K_2=0$ or $K_2\neq 0$, respectively. Interestingly, if $K_2=0$ the fitting parameter K_1 is related to the q parameter in the Kwei equation by [26]:

$$q=kK_1(T_{g2}-T_{g1})/(\omega_1+k\omega_2)^2 \qquad (10)$$

The parameters K_1 and K_2 in the Schneider equation are both related to the difference of T_gs of the blend components, since a normalizing factor $1/(T_{g2}-T_{g1})$ is included in both constants. If this factor is eliminated, two system-specific constants become[22]:

$$\Gamma_1=K_1(T_{g2}-T_{g1}) \qquad (11a)$$

$$\Gamma_2=K_2(T_{g2}-T_{g1}) \qquad (11b)$$

EXPERIMENTAL

Table 3 describes the polymers and random copolymers used in this study and the sources from which they were obtained.

Polymer blends were prepared by casting solutions containing 2% total polymer in methyl ethyl ketone onto glass plates at room temperature. After drying the blends at room temperature, they were dried in a vacuum oven at 353 K for 1 day, heated at 423 K for 3 h and then slowly cooled to room temperature. This procedure led to the same T_g value for PVPh as that obtained with the initial dried powder.

The T_gs and other thermal characteristics of the blends were determined using a Perkin-Elmer DSC-2C apparatus equipped with a TADS microcomputer and calibrated with indium. The T_gs were recorded at the half-height of the corresponding heat capacity jump employing a heating rate of 20 K min^{-1}, on a second scan. In the first one, the samples were heated at a rate of 40 K min^{-1} from room temperature to 423 K, kept at this temperature for 3 min and finally quenched at a nominal rate of 320 K min^{-1}. This procedure was necessary to assure well defined and reproducible transitions. In all cases, the width of the glass transition region was expressed as the difference in temperature between the upper and lower points of deviation from the extrapolated liquid and glassy base lines, respectively.

Thin films of the blends prepared for the Fourier transform infra-red (*FT*i.r.) measurements were cast from 1% (w/v) methyl ethyl ketone solutions onto potassium bromide windows at room temperature. The drying conditions were identical to those used for d.s.c. measurements. All the films studied were sufficiently thin to be within the range where the Beer–Lambert law is obeyed. I.r. spectra were recorded on a Nicolet 5 DXC spectrophotometer. A minimum of 64 scans was signal averaged at a resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

The characterization of the random copolymers used in this study is shown in *Table 3*. The T_g and the heat capacity change at the transition for the copolymers are both in good agreement with calculated data based on weight fraction additivity of the corresponding homopolymer values.

All the binary blends between PVPh and methacrylic homopolymers or copolymers give miscible systems according to the single T_g criterion. *Figure 1* shows the T_g–composition data for the four blends, the predictions of the Couchman–Karasz equation and the additivity rule. As can be seen, all the blends have positive deviations relative to the additivity rule and, generally, experimental data lie between this and the Couchman–Karasz predictive equation. It appears that blends with high methyl methacrylate (MMA) content are better

Table 3 Description of polymers and random copolymers used

Polymer	M_w	T_g(K)[a]	ΔC_p(cal g^{-1} K^{-1})[a]	Source
Poly(*p*-vinyl phenol) (PVPh)	30 000[b]	428	0.098	Polysciences Inc.
Poly(methyl methacrylate) (PMMA)	108 000[a]	391	0.053	Diacom Acrylic, ICI
Poly(ethyl methacrylate) (PEMA)	310 000[c]	352	0.035	Elvacite 2042
Poly(ethyl methacrylate-*co*-methyl methacrylate, 40:60) [EMA-*co*-MMA(60)][d]	435 000[a]	377	0.047	Polysciences Inc.
Poly(ethyl methacrylate-*co*-methyl methacrylate, 30:70) [EMA-*co*-MMA(30)][d]	370 000[a]	365	0.038	Polysciences Inc.

[a] Determined experimentally in this laboratory
[b] Provided by supplier
[c] Ref. 27
[d] Weight per cent MMA in the copolymer

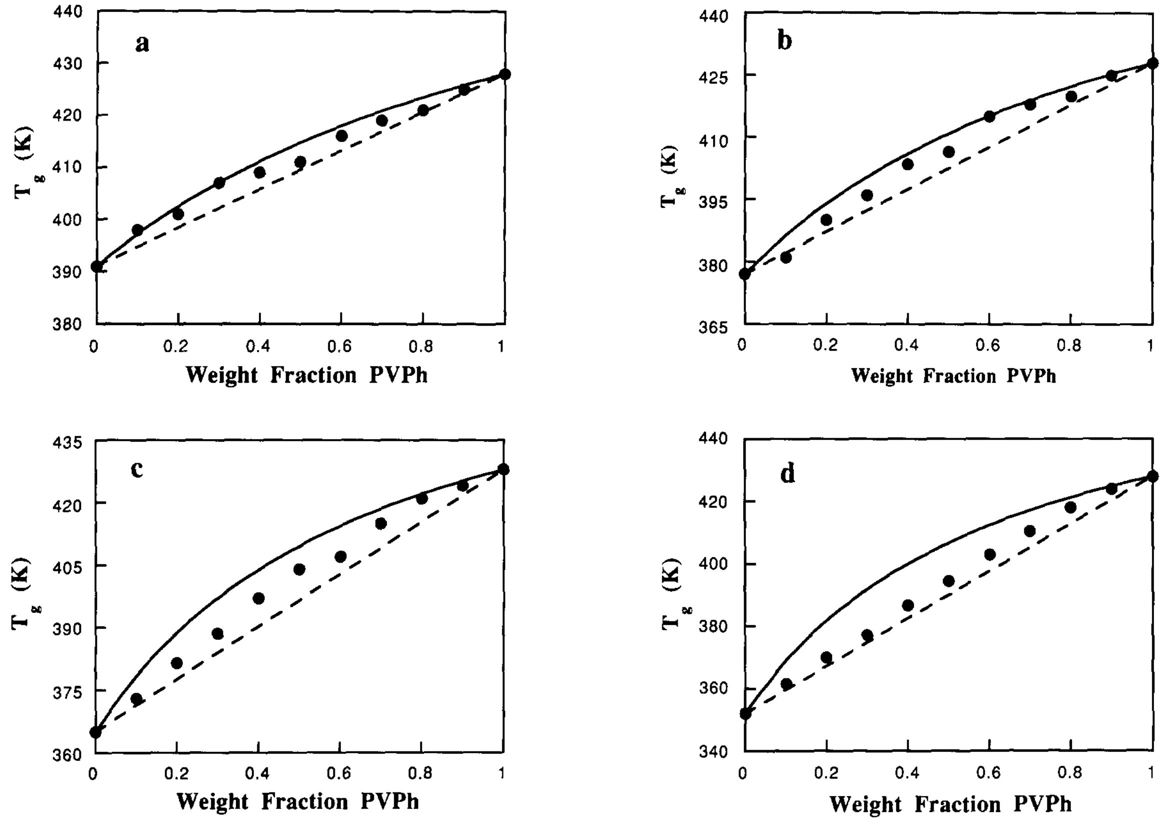

Figure 1 Composition dependence of the T_g for the blends: (a) PVPh/PMMA; (b) PVPh/EMA-*co*-MMA(60); (c) PVPh/EMA-*co*-MMA(30); (d) PVPh/PEMA. Continuous line is the Couchman–Karasz prediction and broken line is the additivity rule. Experimental data are represented by points

represented by the last equation although the fit is not very good. One possible explanation is that the Couchman–Karasz equation considers ΔC_{pi} independent of temperature[28] and also does not take into account the interaction between blend components[29]. In this case, the literature[8,9] recommends the use of the Gordon–Taylor equation with the k parameter treated as an empirical fitting constant that accounts for the interaction between the components. The data are represented in *Figure 2* using the linearized logarithmic version of this equation [see equation (3)]. In *Table 4* a comparison is made between the k parameters so obtained and those assigned by different theories with the physical meaning given in *Table 2*. The k adjustable values deviate considerably from the several values proposed and interestingly, they are almost identical with each other (only a lower value in the PVPh/PEMA blend is observed). If the k adjustable parameter reflects the relative strength of the interactions[8], this implies almost constant values in the blends studied here. One can examine this further by means of *FT*i.r. spectroscopy. The main intermolecular interaction involved in this kind of system is hydrogen bonding between phenolic hydroxyls of PVPh and carbonyl group of polymethacrylates as demonstrated by Moskala *et al.*[30]. We can obtain a measure of the relative strength of these hydrogen bonding interactions using the frequency difference ($\Delta\nu$) between the free (non-hydrogen-bonded) hydroxyl groups (3525 cm^{-1}) and those hydrogen bonded to carbonyl groups. It has been shown that a linear correlation exists between $\Delta\nu$ and the enthalpy of hydrogen bond formation[31]. The hydroxyl absorbance region of the *FT*i.r. spectra for these blends is compared in *Figure 3*. All of the blends studied showed practically identical $\Delta\nu$; this behaviour reflects a similar hydrogen-bonding environment for all these systems, pointing out a constant average intensity of the intermolecular interaction in these systems.

Goh and Siow[27] using a low molecular weight PVPh ($M_w = 1500$) examined the miscibility of PVPh with the polymethacrylate family showing that the miscible blends PVPh/PMMA, PVPh/PEMA, PVPh/poly(n-propyl methacrylate) (PnPMA) and PVPh/poly(iso-propyl methacrylate) (PiPMA) can be described by the Gordon–Taylor equation. The k average adjustable parameter obtained for the above systems is 1.5 ± 0.3. This result is in agreement with the prediction of Painter *et al.* that the strength of the intermolecular interaction is not dependent upon the PVPh molecular weight employed and that it is constant for the polymethacrylate family. The idea was extracted from the association model[32,33] developed by these authors to predict the phase behaviour of polymer blends with *FT*i.r. information.

A measure of the strength of interactions between the components can also be obtained by the width of the glass transition region[34,35]. A glass transition broadening is attributed to concentration fluctuations, so if weak interactions are present, larger equilibrium composition fluctuations are expected than in the case of specific forces. Some type of normalization form for the width of the transition to take into account the diverse potential breadths is very useful. The following expression is used for the corrected width, W_c:

$$W_c = \Delta W / \Delta W_{\max} \qquad (12)$$

where ΔW is the difference between the experimental width and the additive one and $\Delta W_{\max}$ represents the potential width minus the additive breadth. The potential width here is the difference between the end point of the

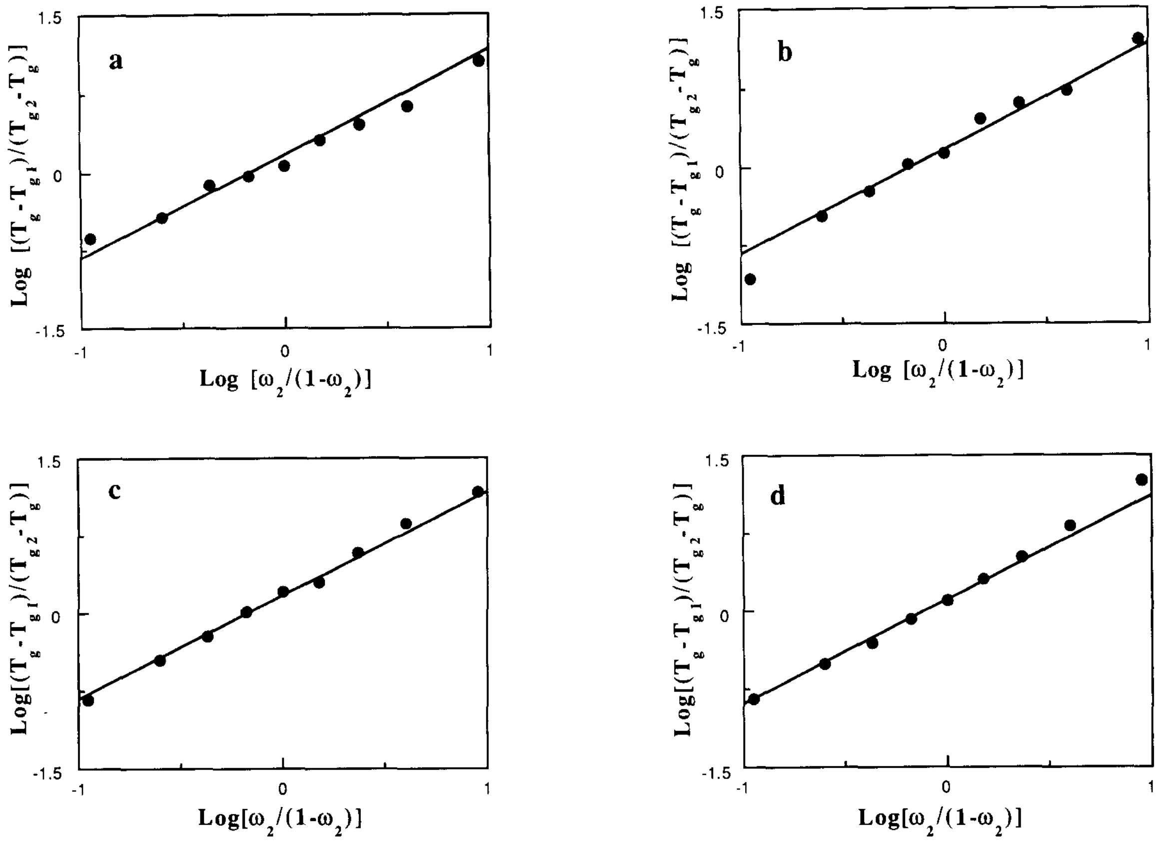

Figure 2 Composition dependence of the T_g according to the linearized Gordon–Taylor equation for the blends: (a) PVPh/PMMA; (b) PVPh/EMA-*co*-MMA(60); (c) PVPh/EMA-*co*-MMA(30); (d) PVPh/PEMA

Table 4 Comparison between the k adjustable parameter and different theoretical interpretations given in the literature

System	Adjustable parameter	$\Delta C_{p2}/\Delta C_{p1}$	$\gamma_2 m_1/\gamma_1 m_2$ [a]	T_{g1}/T_{g2}
PVPh/PMMA	1.5	1.87	0.83	0.91
PVPh/EMA-*co*-MMA(60)	1.5	2.11	0.80	0.88
PVPh/EMA-*co*-MMA(30)	1.5	2.61	0.78	0.85
PVPh/PEMA	1.3	2.83	0.76	0.82

[a] γ_i values of 4 and 5 were employed for PMMA and PEMA, respectively, according to Di Marzio[18]. A value of 4 was chosen for PVPh

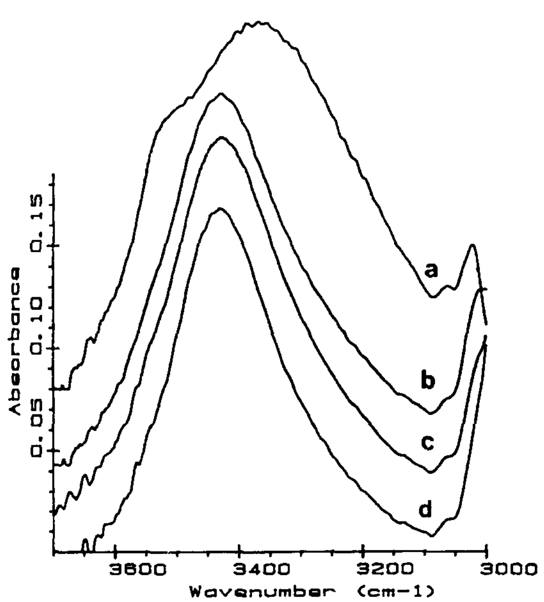

Figure 3 Hydroxyl stretching region of the *FT*i.r. spectra for: (a) PVPh; (b) PVPh/PMMA 50:50; (c) PVPh/EMA-*co*-MMA(30) 50:50; (d) PVPh/PEMA 50:50

transition region for the higher T_g component minus the onset temperature for the lower T_g component[34]. One can see that W_c is zero if the experimental width equals the additive breadth, whereas, a value unit is obtained for blends with the maximum potential width.

The corrected widths of the glass transition region for the blends are represented in *Figure 4*, showing an enlargement of the transition zone for middle compositions (the maximum value is actually at 0.4 weight fraction PVPh in the blend). Since W_c is far apart from the maximum potential value ($W_c = 1$) only small concentration fluctuations will be present in these blends. The W_c behaviour is nearly the same in all the blends and no real systematic trend with methyl methacrylate content in the copolymer can be ascertained. Consequently, according to the transition width criterion, local composition fluctuations will be very similar in the homopolymer and copolymer blends with PVPh. It seems that this criterion is not sensitive enough to detect the copolymer effect at less for this system.

Additional information about the state of stabilization in blends can be ascertained by means of the Kwei

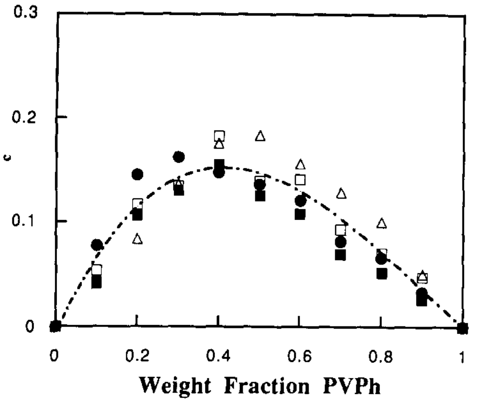

Figure 4 Corrected width of the glass transition region as a function of composition for blends of PVPh and (□) PMMA, (△) EMA-*co*-MMA(60), (●) EMA-*co*-MMA(30) and (■) PEMA

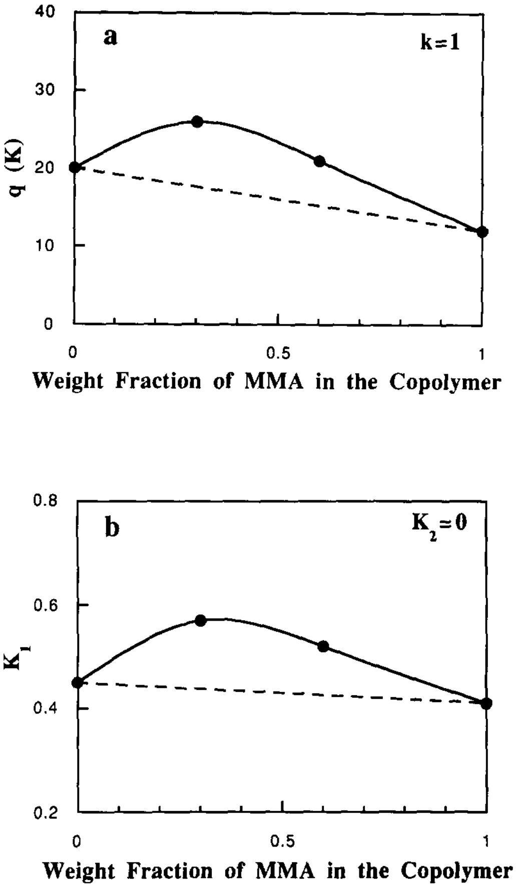

Figure 5 Dependence on MMA copolymer content of the q parameter in the Kwei equation (a) and the K_1 related constant in the Schneider equation (b) for the PVPh/EMA-*co*-MMA system. The continuous and broken lines were drawn as visual guides only

equation through the q parameter. Thus, the T_g–composition data were fitted according to equation (5) because the k values obtained with equation (4) were nearly unity. Similar k values (1.09 ± 0.06) were derived previously for blends with polymethacrylate homopolymers using the low molecular weight PVPh[27]. Following Lin *et al.*[21], when $k=1$, the q parameter is a measure of the reduction ($q<0$) or increase ($q>0$) of the energy barrier to backbone movement in the blend and represents the excess stabilization energy with respect to the mean of the stabilization energies of the pure components. The sources of backbone stabilization are ultimately the contacts between the main chain and its environments. So far our PVPh/copolymer blends q can be related to hydrogen bond formation and to changes in the environment of the chains[21,36]. In this sense, the stabilization due to the dilution of repulsive interactions might also be reflected in this parameter. The dependence of the q parameter on the MMA copolymer content in the blends is represented in *Figure 5a*. The q values for the copolymer blends are higher than those predicted by additivity. This fact suggests the presence of the copolymer repulsion effect in this system. Since q in Kwei's equation is related to the K_1 parameter in Schneider's equation (setting $K_2=0$), similar trends are obtained for the latter equation as represented in *Figure 5b* employing equations (8) and (9).

Following the analysis of glass transition data to obtain an indication of the extent of miscibility and the presumed copolymer repulsion effect, the Schneider equation was used. In *Figure 6* the T_g–composition data are represented using equations (8) and (9). The left-hand side of equation (9) is very sensitive to experimental errors if both the difference ($T_g - T_{g1}$) and ω_{2C} are low. Consequently, ω_{2C} values <0.1 have not been considered. In general, curved representations are obtained for systems with both K_1 and K_2 not equal to zero. The K_1 parameter shows a positive deviation from additivity when it is plotted against the MMA copolymer content. The K_2 constant lies on the additivity line. The magnitudes of the K_1 and K_2 parameters in these blends are similar to those obtained in the Novolac/PMMA and polydonor/polyacceptor blends by Brekner *et al.*[19]. As pointed out earlier, K_1 and K_2 are related to the difference in T_gs of the blend components ($T_{g2} - T_{g1}$), so the Γ_1 and Γ_2 parameters have been employed as suggested by Brekner *et al.*[22]. Claims were made by these authors about the interdependence between Γ_i parameters and thermodynamic blend properties. A linear correlation between both Γ_1 and Γ_2 constants and the enthalpy of mixing was observed in polydonor/polyacceptor blends[22]. *Figure 7* shows the dependence of Γ_1 and Γ_2 normalized parameters on MMA copolymer content. One can see that the parameters are greater for the PVPh/PMMA blend than for the PVPh/PEMA one and the copolymer blends show positive deviations from the additivity of the component values taking into account the copolymer composition. If Γ_i parameters are also related to the heat of mixing in the systems studied here, this suggests both an increased contribution for the copolymer with respect to homopolymer blends and a higher value in the PVPh/PMMA blends than in the PVPh/PEMA system. This result is in agreement with *FT*i.r. and d.s.c. measurements showing a decrease of the miscibility as the size of the pendant alkyl group increased[10,27].

Thus, we can conclude that, based only on glass transition behaviour, the Schneider equation and the Kwei equation are useful tools to obtain information about the extent of mixing and might reflect the additional stabilization caused by repulsive interactions in copolymer blends. Further studies are needed to support the so-called copolymer repulsion effect as another mechanism of interaction in the PVPh/EMA-*co*-MMA system. Nevertheless, some equations employed in this work to model the thermal behaviour insinuate this phenomenon.

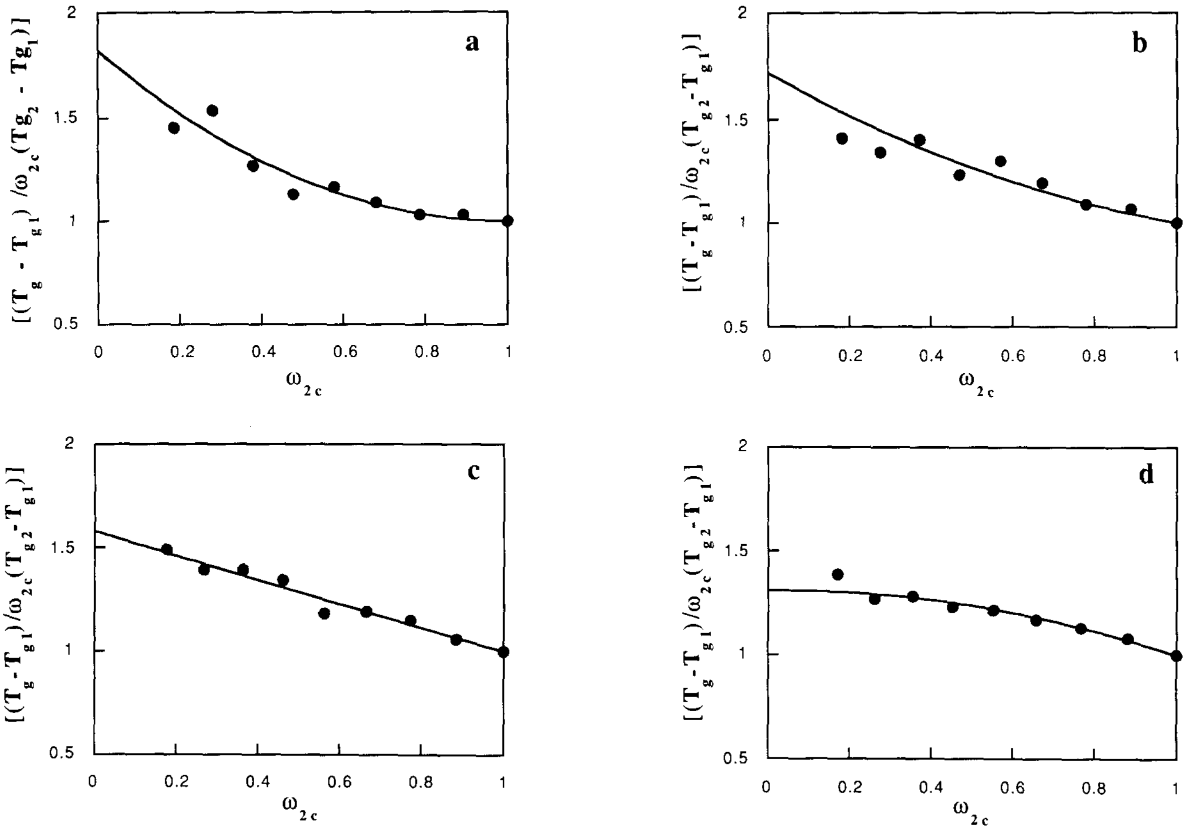

Figure 6 Composition dependence of the T_g according to the Schneider equation for the blends: (a) PVPh/PMMA; (b) PVPh/EMA-*co*-MMA(60); (c) PVPh/EMA-*co*-MMA(30); (d) PVPh/PEMA

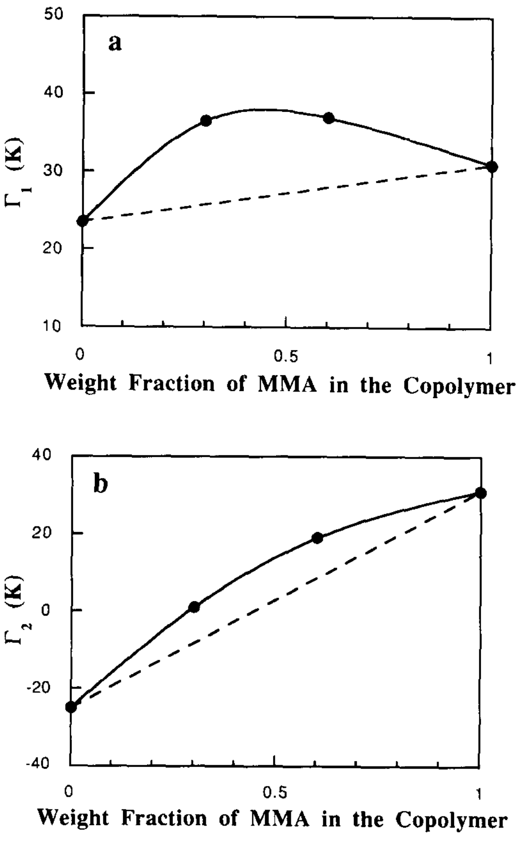

Figure 7 Dependence on MMA copolymer content of Γ_1 and Γ_2 parameters in the Schneider equation. The continuous and broken lines were drawn as visual guides only

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