Analysis of the Glass Transition Temperature of Miscible Polymer Blends

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ABSTRACT: The miscibility of polymer blends is often assessed by the measurement of a single glass transition temperature (T_g) as a function of composition. T_g–composition data are generally expressed with equations which predict a monotonic variation of T_g, and any deviation of the results from the linear behavior is then considered as a measure of the strength of the interactions involved. However, an examination of the T_g data of polymer mixtures reveals that several systems exhibit a cusp as a function of composition. In the framework of the free volume theory, this behavior was shown several years ago by Kovacs to occur. According to this theory, if the free volume of the high-T_g polymer goes to zero at a critical temperature T_c, above the T_g of some of the blends, Kovacs's equation can be used; above T_c, the classical T_g–composition equations can be used. This sort of analysis was applied to a series of blends made of poly(ϵ-caprolactone) with chlorinated polymers, with a good agreement with the experimental results and good predictions of T_c and ϕ_c, the critical volume fraction. Interaction parameters between this polyester and chlorinated polymers were then determined.

Introduction

The miscibility of binary polymer blends is often ascertained by the measurement of their glass transition temperature (T_g). In general, it is observed that T_g increases monotonically as a function of composition, with a more or less pronounced negative deviation from linearity.

Several theoretical equations have been proposed to explain the T_g–composition behavior of those blends, as we will see in the following section. However, these expressions do not lead to a break (or cusp) in the curve which may often be observed experimentally when the T_g's of the two polymers considered are separated by more than 52 deg.

It is then the purpose of this article to show that miscible binary polymer blends made of poly(ϵ-caprolactone) and chlorinated polymers often exhibit a cusp in their T_g–composition dependence and that this behavior can be predicted satisfactorily with a free volume theory initially developed by Kovacs.

Theory

Over the years, numerous equations have been proposed to express the T_g–composition dependence of miscible polymer blends. These equations have been derived from the so-called free volume hypothesis or from thermodynamic arguments, assuming the continuity of the entropy of the mixture at T_g.

The more general of these equations is due to Couchman and Karasz[1] and it reads, for a binary mixture, assuming that ΔC_{pi} does not depend on temperature:

$$\ln T_g = \frac{W_1 \Delta C_{p1} \ln T_{g1} + W_2 \Delta C_{p2} \ln T_{g2}}{W_1 \Delta C_{p1} + W_2 \Delta C_{p2}} \qquad (1)$$

T_g is the glass transition temperature of the blend, W_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}.

One interesting point is that eq 1 can be reduced to several other equations which have been proposed for the same purpose, following a certain number of simplifying assumptions.[2,3]

If it is assumed that $\Delta C_{p1} = \Delta C_{p2}$, then

$$\ln T_g = W_1 \ln T_{g1} + W_2 \ln T_{g2} \qquad (2)$$

which was proposed by Pochan et al.[4]

If, furthermore, T_{g2}/T_{g1} is not very far from unity, then the logarithm expansion of eq 2 can be limited to the first term, and one finds the rule of mixtures:

$$T_g = W_1 T_{g1} + W_2 T_{g2} \qquad (3)$$

Assuming again that $\Delta C_{p1} = \Delta C_{p2}$, after rearrangement and expansion of the logarithm term of eq 2, one finds the Fox equation:

$$T_g^{-1} = W_1/T_{g1} + W_2/T_{g2} \qquad (4)$$

If, instead of setting $\Delta C_{p1} = \Delta C_{p2}$, which is not a good approximation, one is a little more general and writes $\Delta C_{p1}/\Delta C_{p2} = k$, a constant, then

$$\ln T_g = \frac{W_1 \ln T_{g1} + k W_2 \ln T_{g2}}{W_1 + k W_2} \qquad (5)$$

an expression proposed by Utracki.[5] In the special case where k is equal to unity, one comes back to eq 2.

Finally, with the first term of the expansion of the logarithm of eq 1 and if T_{g2}/T_{g1} is close to unity, then

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} \qquad (6)$$

where $k = \Delta C_{p2}/\Delta C_{p1}$, which is the Gordon–Taylor equation (6) if k is defined by $\Delta\beta_2/\Delta\beta_1$, where $\Delta\beta_i$ is the cubic expansion coefficient of polymer i. Of course, setting $\Delta C_{p1} = \Delta C_{p2}$ leads, again, from eq 6, to eq 3.

It is then seen that eq 3 and 4 are crude approximations to eq 1; eq 2, 5, and 6 are certainly more general, particularly eq 5 and 6, which take into account the ratio of the specific heats of the two samples.

However, with or without approximations, each of these equations predicts a monotonic dependence of T_g upon concentration. This is illustrated in Figure 1 for a specific example where T_{g1} = 205 K (this can be poly(caprolactone) (PCL)), T_{g2} = 357 K (this can be poly(vinyl chloride) (PVC)), ΔC_{p1} = 0.565 J/g·K (a reasonable value for PCL), and ΔC_{p2} = 0.322 J/g·K (the PVC value of ref 5). It should be noted that these parameters give a constant value of $T_{gi}\Delta C_{pi}$ of 115.5 J/g, which is the value generally accepted.[3,5,7,8] Figure 1 shows that each of these equations gives a curve which lies below the straight line predicted by eq 3.

The difference between the predictions of those equations is relatively small, the deviation from linearity (eq 3), increasing when going from eq 2 to eq 4, 6, 1, and 5, in that order. When the k parameter of eq 5 and 6 is taken

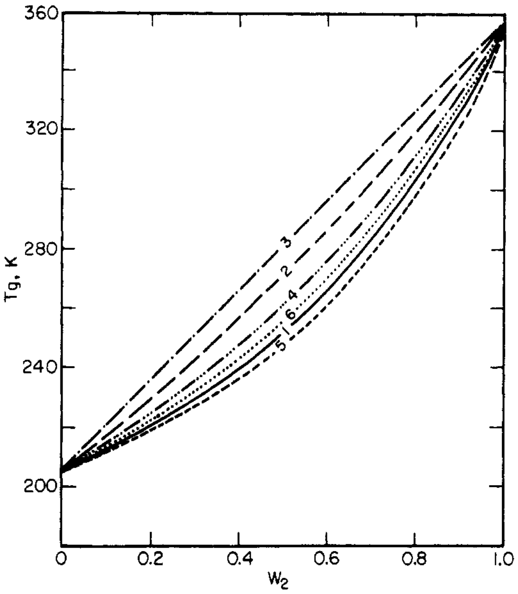

Figure 1. Theoretical glass transition temperature of PCL/PVC blends as a function of weight fraction of PVC according to equations proposed by Couchman and Karasz (1), Pochan et al. (2), Fried et al. (4), Utracki (5), and Gordon–Taylor (6); (3) corresponds to the rule of mixtures.

as an adjusting parameter, as is often done in the literature, then experimental data can be reasonably well fitted whatever their deviation from linearity. Of course, the same result can be achieved by using eq 1 if one or both ΔC_{pi} values are taken as adjusting parameters. Again, the important point of Figure 1 is that the same kind of behavior is predicted by each of these equations and none of them allow for the presence of a break.

However, an examination of some of the data of the literature and of our laboratory indicates, at least in some cases, the presence of a break (or cusp) as a function of composition. In fact, Roy et al.[9] have already shown that the T_g data of PVC plasticized with benzyl butyl phthalate exhibit a cusp at $T_c = 303$ K and $\phi_1 = 0.25$ (plasticizer concentration). Similar cusps have been reported in the literature with other polymer–plasticizer systems.[3,10] More recently, Nandi et al.[11] have also mentioned, in a brief note and using some of our published data, that a cusp is sometimes found in polymer blend mixtures. It is the purpose of this article to show that this situation appears to be general with poly(ϵ-caprolactone)/chlorinated polymer blends under the conditions described below.

This behavior has been shown to occur by Kovacs,[12] several years ago, in the framework of the free volume theory. According to this theory, if the difference ($T_{g2} - T_{g1}$) between the two homopolymers involved is larger than about 50 deg, the free volume of polymer 2 becomes zero at a critical temperature T_c, and then equations based on the free volume theory, such as eq 2–6, become invalid below T_c because it would imply a negative free volume, which is impossible. This critical temperature, and the corresponding critical volume fraction ϕ_c (relative to polymer 1), have been calculated by Kovacs:[12]

$$T_c = T_{g2} - (f_{g2}/\Delta\alpha_2) \quad \text{if} \quad T_{g2} > T_{g1} \tag{7}$$

$$\phi_c = f_{g2}/[\Delta\alpha_1(T_{g2} - T_{g1}) + f_{g2}(1 - \Delta\alpha_1/\Delta\alpha_2)] \tag{8}$$

where f_{g2} is the free volume fraction of polymer 2 at T_{g2} and $\Delta\alpha_2$ the difference between the volume expansion coefficients in the glassy and liquid states.

Below T_c, Kovacs[12] has shown that T_g is given by

$$T_g = T_{g1} + (f_{g2}/\Delta\alpha_1)(\phi_2/\phi_1) \tag{9}$$

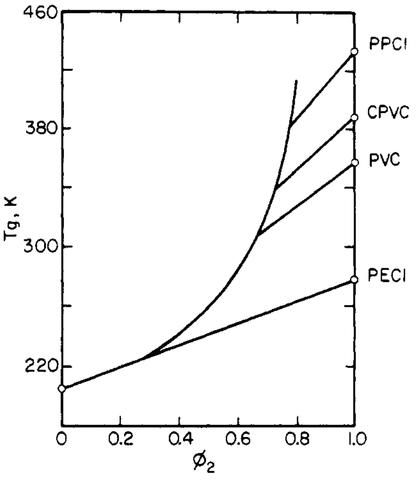

Figure 2. Theoretical glass transition temperatures of PCL/chlorinated polymer blends as a function of volume fraction of chlorinated polymer; eq 3 is used below ϕ_c; eq 9 is used above.

According to this equation, T_g depends uniquely upon the parameters of polymer 1 (T_{g1}, $\Delta\alpha_1$, and ϕ_1), if f_{g2} is given the usual value of 0.025. It assumes that there is no excess volume between the two polymers upon mixing. If the excess volume is not negligible, Braun and Kovacs[13] have modified the initial theory to read

$$T_g = T_{g1} + \frac{\phi_2 f_{g2} + g\phi_1\phi_2}{\phi_1\Delta\alpha_1} \tag{10}$$

which is again valid below T_c. In this equation, g is an interaction term which is defined by

$$g = (V_e/V)/\phi_1\phi_2 \tag{11}$$

where V is the volume of the blend sample and V_e the excess volume. V_e (and g) is positive if blend interactions are stronger than the average interactions between molecules of the same species, and it is negative otherwise.[13]

This theory then gives a break (or cusp) in the T_g–composition curve of miscible polymer blends when $T_c > T_{g1}$. This behavior is illustrated in Figure 2 for blends of PCL with a chlorinated poly(ethylene) (PECl) ($T_{g2} = 278$ K), PVC, chlorinated PVC (CPVC) ($T_{g2} = 388$ K), and chlorinated poly(propylene) (PPCl) ($T_{g2} = 433$ K). At low chlorinated polymer concentrations, the same curve (eq 9) is drawn whatever the chlorinated polymer considered: it depends uniquely upon parameters of polymer 1 (PCL). At high chlorinated polymer concentrations, a different curve is generated for each polymer by using eq 3. Since $f_{g2} = 0.025$ and with the classical value of 0.00048 K^{-1} for $\Delta\alpha_2$, $T_c = (T_{g2} - 52)$, which gives 381, 336, 305, and 226 K for PPCl, CPVC, PVC, and PECl, respectively; the corresponding ϕ_c are 0.23, 0.28, 0.35, and 0.71, respectively (relative to polymer 1). Therefore, a large difference between T_{g2} and T_{g1} leads to the appearance of a break in the T_g–composition curve; moreover, the larger this difference, the smaller the concentration range where eq 3 applies. However, with PECl and a difference of only 73 K between T_{g2} and T_{g1}, the break is hardly noticed.

Experimental Section

Table I gives the list of the polymers used in the present study, their weight-average molecular weights, M_w, and glass transition temperature (T_g).

Blends were prepared by slowly casting films from tetrahydrofuran (THF) solutions. The resulting films were dried under vacuum for at least 5 weeks. Films thicknesses were between 20 and 30 μm.

Differential scanning calorimetry (DSC) was conducted with a Perkin-Elmer DSC-4 apparatus equipped with a TADS mi-

Table I
Polymers Used

polymer		T_g, K	M_w, kg/mol	supplier
poly(ϵ-caprolactone)	PCL	205	20	Aldrich
poly(vinyl chloride)	PVC	355	80	Shawinigan
chlorinated PVC (67.2 wt % Cl)	CPVC	388	119	B. F. Goodrich
chlorinated poly(propylene)	PPCl	433	57	Aldrich
poly(chlorostyrene)	PSCl	398	99	Aldrich
poly(vinyl bromide)	PVB	323	30	this lab.
chlorinated poly(ethylene) (48 wt % Cl)	PECl	278	117	Aldrich

Table II
Data Used in the Analysis of PCL/PVC Mixtures

wt % PVC	% crystallinity	ϕ_2	T_g, K
0.00	63.1	0.00	205
0.10	63.0	0.19	222
0.15	59.5	0.26	230
0.20	58	0.32	237
0.25	55.9	0.37	242
0.30	51.6	0.41	252
0.35	48	0.45	254
0.40	42.3	0.48	266
0.50	25.1	0.51	261
0.55	0	0.49	265
0.60	0	0.54	279
0.70	0	0.65	294
0.80	0	0.76	317
0.90	0	0.88	338
1.00			357

crocomputer. The DSC apparatus was calibrated with ultrapure indium. The T_g's reported in this article were recorded at the half-height of the corresponding heat capacity jump.

For PCL/PSCl, PCL/PPCl, PCL/PVB, and PCL/PECl blends, we used data that we have already published.[14-16] For the other systems, we have made our own measurements in order to make sure that each system has been submitted to a similar thermal treatment. These measurements were taken as follows: in the DSC apparatus, the samples were first heated up to 423 K and maintained 10 min at that temperature to remove the last traces of solvent remaining in the films. Then the samples were cooled down to 173 K. For samples with slow crystallization rates (those containing 80–50% PCL), the cooling rate was 5 K/min, between 323 and 233 K, in order to allow sufficient time for the crystallization. Outside this temperature range and for the other blends at any temperature, the cooling rate was 20 K/min. Glass transition temperatures, melting temperatures, and enthalpies of fusion were subsequently recorded at a heating rate of 40 K/min. Degrees of crystallinity were calculated by taking the ratio of the enthalpy of fusion measured to the enthalpy of fusion of pure PCL crystal, 139.5 J/g.[20]

Results

We have decided to gather a new series of data for the PCL/PVC system, instead of using literature values, to make sure that the crystallization of PCL is well controlled and its degree of crystallinity accurately known. Table II gives the T_g values obtained as a function of composition. When they are plotted as a function of the PVC weight fraction W_2, they agree, as shown in Figure 3, with the data obtained by other authors.[17-19] At high PCL concentrations, the T_g's obtained in this study are slightly higher, due to the method of preparation used and to higher degrees of crystallinity; Koleske and Lundberg, Robeson, and Hubbell and Cooper used quenched samples.

From the degree of crystallinity measured (Table II), the real composition of the amorphous phase of each blend was calculated, as well as its volume fraction ϕ_2, using a value of density of 1.095 g/cm^3 for amorphous PCL[20] and 1.395 g/cm^3 for PVC.[21] T_g is then plotted as a function of ϕ_2 in Figure 4. A break (or cusp) is seen in this curve. Using the values of f_{g2} and $\Delta\alpha_2$ given by the iso-free volume theory, values of T_c and ϕ_c of 305 K and 0.34 are calculated, respectively. Equation 9 is then used to simulate the bottom part of the diagram, and eq 3 the top part (Figure 4). The calculated line at low temperatures falls slightly below the experimental data. In order to have a better agreement between theory and experiment, eq 10 was then used instead of eq 9 and fitted to the data points with a g parameter of 0.010 (Table III).

Similarly, the data gathered previously[16] with PCL/CPVC blends were corrected to take into account the

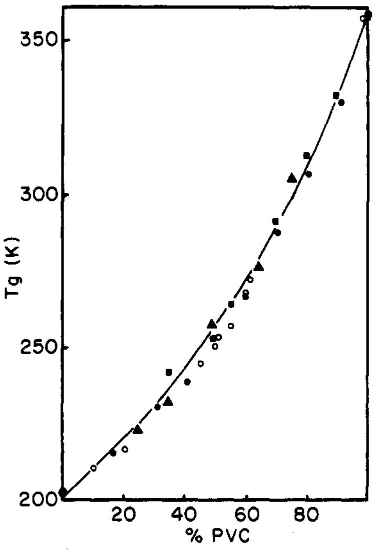

Figure 3. Uncorrected glass transition temperature of PCL/PVC blends as a function of weight fraction PVC; data taken from Koleske and Lundberg (●), Robeson (○), Hubbell and Cooper (▲), and our Laboratory (■) (ref 17, 18, 19, and 22, respectively).

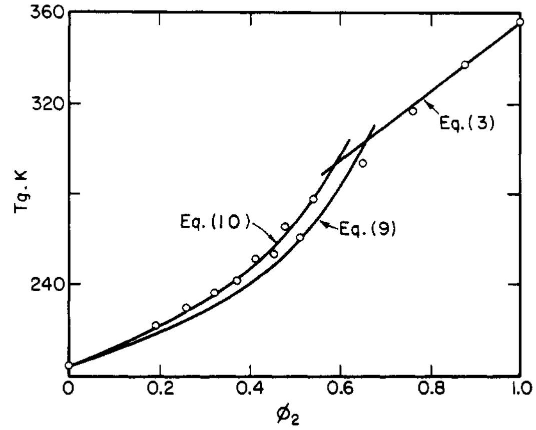

Figure 4. Glass transition temperature of PCL/PVC blends as a function of volume fraction of PVC.

Table III
Kovacs' Analysis of T_g–Composition Data in Blends with PCL

T_g, K of halogenated polym		eq 10		
		T_c, K	ϕ_c	g
PPCl	433	350	0.30	0.005
CPVC	388	322	0.38	0.020
PVC	357	293	0.41	0.010
PECl	278	225	0.63	–0.015[a]
PSCl	388	318	0.28	–0.020
PVB	323	290	0.30	–0.015

[a] Calculated from eq 12.

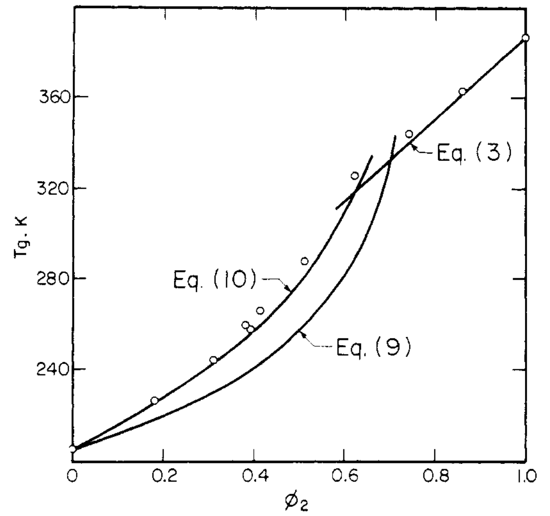

Figure 5. Glass transition temperature of PCL/CPVC blends as a function of volume fraction of CPVC.

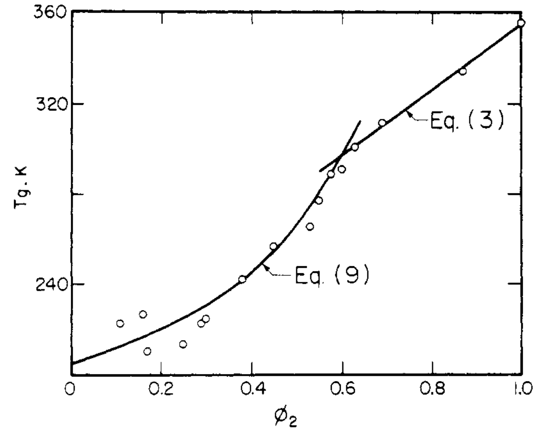

Figure 6. Glass transition temperature of PCL/PVC/CPVC ternary blends as a function of volume fraction of the chlorinated polymers (PVC + CPVC).

crystallinity of PCL. After this correction, the data, which are shown in Figure 5, clearly show a cusp. The upper part of the curve is fitted with eq 3 and the lower one with eq 9. Again, the theoretical line falls below the data points. Equation 10 is then found to give better agreement with experiment with a g value of 0.020. Also, the ternary system PCL/PVC/CPVC was analyzed in the case where $\phi_{\mathrm{PVC}} = \phi_{\mathrm{CPVC}}$.[22] This time, eq 9 satisfactorily fits the data (Figure 6), meaning that $g = 0$; at low PCL concentrations, no data are reported because there is incomplete miscibility at those compositions and two T_g's were recorded;[22] in other words, in that range, the PCL concentration is too low to eliminate the strong repulsive forces between PVC and CPVC.

To complete the analysis, Figure 7 gives an example where a negative g value is required to fit the data. These experimental values were obtained for PCL/PVB mixtures.[15] They clearly exhibit a cusp, as the previous examples. However, this time, eq 9 gives a line which is above the experimental values; the data can, however, be satisfactorily expressed by eq 10 with $g = -0.015$. This negative sign means that the average interactions between blend components are weaker than those between molecules of the same species. This conclusion is consistent with the borderline miscibility reported previously for this blend.[15,23]

Two other systems of the same series were also analyzed with eq 10. As shown in Table III, PCL/PPCl mixtures[14] give $g = 0.005$ while PCL/PSCl blends give $g = -0.020$.

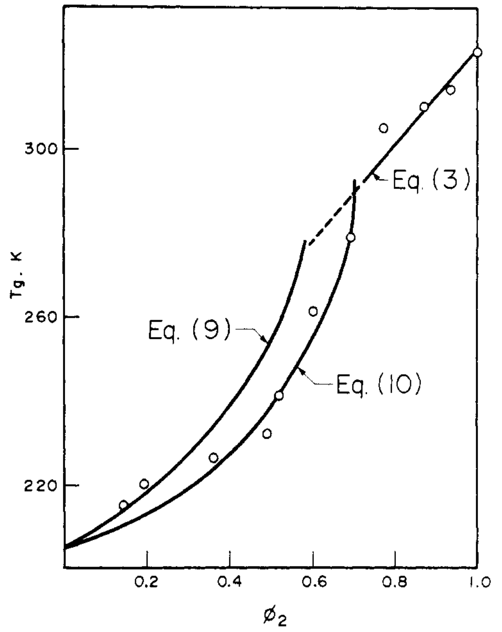

Figure 7. Glass transition temperature of PCL/PVB blends as a function of volume fraction of PVB.

Discussion and Conclusions

A careful analysis of PCL/chlorinated polymer T_g data, after correction for the crystallinity of PCL, reveals that the T_g-composition variation is not monotonic but exhibits a cusp, similar to that observed with polymer/diluent mixtures.[3,9,10,12,13] In contrast, the classical equations proposed by Couchman, Pochan, Utracki, Gordon–Taylor, Fried, and co-workers[1-6] predict a monotonic variation of T_g as a function of composition, in disagreement with the results shown in this paper. It is shown that the cusp observed experimentally can be explained by a free volume theory proposed by Kovacs several years ago.[12] In the framework of this theory, at $T < T_c$, the free volume of the high-T_g polymer would be negative by classical free volume equations, which is impossible. Kovacs has then proposed, below T_c, a new equation which gets around this problem. At the same time, above T_c, eq 1–6 apply satisfactorily, although it is very difficult to differentiate between them because the concentration range where data are available is limited and the accuracy of the data is low.

Using Kovacs' theory, we note in Table III that

$$g(\mathrm{CPVC}) > g(\mathrm{PVC}) > g(\mathrm{PECl})$$

meaning that the interactions between PCL and CPVC are stronger than those between PCL and PVC, which are in turn stronger than those between PCL and PECl, in agreement with our earlier suggestion.[16,24] This trend is also in agreement with a more negative χ parameter between PCL and CPVC than between PCL and PVC, noted in a study of ternary mixtures.[22] This tendency can be explained by the higher chlorine concentration of CPVC, leading to a larger number of interacting groups between PCL and CPVC than between PCL and PVC; similarly, the number of interacting groups between PCL and PVC is larger than that between PCL and PECL.

In the framework of Kovacs' free volume theory, a cusp begins to appear when $(T_{g2} - T_{g1})$ is large enough. In principle, T_c will be larger than T_{g1} and will show up for a difference between T_{g2} and T_{g1} of 52 K; in practice, the cusp becomes apparent for a difference larger than 70 K. This phenomenon has been undetected so far for polymer–polymer mixtures, except for a note by Roy et al.[11]

for several reasons: the accuracy of the data can be too low; the phenomenon can be masked if the contribution of the crystallinity is not taken into account; or the limited number of data points reported can make its observation ambiguous. However, we believe that the phenomenon can be general when accurate data are used, but this must still be proven. In the case where a cusp appears, it is obvious that eq 1–6, and similar relationships, whatever their origin, cannot satisfactorily express the data. When these are free volume theories, the limitation comes from the flaw in the theory associated with negative free volumes; when these are thermodynamic theories, the limitation must be related to a weak assumption, perhaps the assumption that ΔC_{pi} does not depend on temperature. In any event, Kovacs' theory is the only one which can explain satisfactorily the sort of cusp reported in this paper for polymer/polymer mixtures and those reported elsewhere[3,9,10,12,13] for polymer/diluent mixtures.

A word now concerning the critical temperature T_c which is the temperature where the high-T_g polymer ceases to contribute to the free volume of the mixture. In Kovacs' theory, this temperature corresponds to that, below T_g, where a real second-order transition may be observed, as predicted by Gibbs and Di Marzio.[25] It can also be related, as done by Kovacs,[12] to T_∞ which appears in the WLF equation.[26]

Finally, it is noted that the interaction parameter g of Kovacs' equation can be introduced into the Gordon–Taylor equation. Braun and Kovacs[13] have shown that

$$T_g = \frac{\phi_1 T_{g1} + k\phi_2 T_{g2} + g\phi_1\phi_2}{\phi_1 + k\phi_2} \qquad (12)$$

where volume fractions ϕ_i are used instead of weight fractions W_i. Equations 12 can be used to fit the data above T_c, if a large enough number of accurate data points are available. This method was used in this article to fit the PCL/PECl data and the result of this analysis is consistent with the analyses carried out below T_c with PCL/PVC and PCL/CPVC blends.

Conclusions

We have shown, with several examples taken from the literature, that a cusp is present in the T_g–composition curves of miscible polymer blends if $(T_{g2} - T_{g1})$ is large enough. A free volume theory due to Kovacs[12] can be used to illustrate this kind of behavior with low and high molecular weight plasticizers; this is the only theory that can be used to mimic this behavior.

In that context, the free volume theory is most useful despite its shortcomings. In particular, it is known that the variation of f_2 below T_{g2} is not given by the abrupt variation assumed in Kovacs' theory. However, we have to consider that the use of this theory represents an improvement relative to equations, such as the Gordon–Taylor equation, which assumes implicitely a negative value of f_2 below T_c.[26,27] Moreover, Kovacs' theory leads, in several examples, to a remarkable agreement with the experimental data not only in the qualitative prediction of the presence of a cusp but also in the quantitative prediction of T_c and ϕ_c. However, there is no doubt that a better theory needs at this point to be developed with or without the use of the free volume concept.

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Registry No. PCL (homopolymer), 24980-41-4; PCL (SRU), 25248-42-4; PVC, 9002-86-2; PSCl, 9022-52-0; PVB, 25951-54-6.

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