Miscibility behaviour of ternary poly(caprolactone)/poly(vinyl chloride)/chlorinated poly(vinyl chloride) blends

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From the literature, it is well known that poly(caprolactone)/poly(vinyl chloride) (PCL/PVC) and poly(caprolactone)/chlorinated poly(vinyl chloride) (PCL/CPVC) blends are miscible, at any composition. However, PVC and CPVC are immiscible. It is shown, in this study, that the addition of PCL to a PVC/CPVC mixture allows the observation of a single glass transition temperature (T_g) at PCL contents larger than 40% at high PVC/CPVC ratios and at PCL contents larger than about 26% at low PVC/CPVC ratios. The observation of a single T_g does not necessarily mean that the three polymers form a homogeneous phase, since it can also correspond to the coexistence of two homogeneous binary PCL/PVC and PCL/CPVC phases having close values of T_g. The one-T_g/two-T_g boundary of this ternary mixture was established; it is observed that it is not symmetrical with respect to the PVC and CPVC apexes. This behaviour can be modelled with thermodynamic interaction parameters of -0.3 between PCL and PVC, -1.8 between PCL and CPVC, and $+3.5$ between PVC and CPVC. Finally, a variety of phase behaviour was observed in the ternary diagram region where several T_g values are recorded.

INTRODUCTION

Olabisi[1] has suggested that miscibility between two polymers often results from the 'complementary dissimilarity' of their structures; this suggestion has been confirmed by several authors[2-4]. Two polymers with different structures (i.e. they are dissimilar) are then likely to be miscible if specific interactions of some kind (i.e. a complementary factor) favour homogeneity of the blend. Also, two high-molecular-weight polymers with similar structures, i.e. two polyesters or two chlorinated polymers, can hardly be miscible owing to the absence of an entropic driving force to favour a one-phase structure. In other words, the miscibility of a blend is driven by enthalpic forces.

For example, a large number of aliphatic and aromatic polyesters have been shown to be miscible with chlorinated polymers, including poly(vinyl chloride) (PVC) and chlorinated PVC (CPVC), due to the presence of specific interactions between those structures[2,5-9]. In particular, a hydrogen bond is formed between the carbonyl group of the polyester and the α-hydrogen of PVC[1,10,11]. In addition, several independent studies have shown that poly(ε-caprolactone) (PCL) is more miscible than any other polyester[12-14]. In contrast, PVC and CPVC are completely immiscible: whatever the method of preparation used, i.e. solution or dry blending, two phases are observed by optical microscopy and, in some cases, even with the naked eye, in addition to the classical observation of two glass transition temperatures (T_g) for the homopolymers, except at very low concentrations[15].

In that context, it seems interesting to look at ternary PCL/PVC/CPVC blends to investigate the possibility of improving the miscibility of the two latter components by the addition of PCL. This method is similar to the proposal of using a block copolymer poly-AB to solubilize homopolymers poly-A and poly-B, or to the more recent use of a copolymer poly-CD where poly-C is miscible with poly-A, and poly-D with poly-B[16,17], without the problem of synthesizing a costly block copolymer.

Some ternary blends (with miscible components) have been investigated in the literature. For example, poly(vinylidene fluoride) (PVF$_2$) was used by Kwei *et al.*[18] to solubilize poly(methyl methacrylate) (PMMA) and poly(ethyl acrylate) (PEA). Miscibility was found in the amorphous phase with PVF$_2$ contents between 30 and 70 wt%. Similarly, poly(acrylonitrile-*co*-butadiene) was blended with poly(vinylidene chloride-*co*-vinyl chloride) and poly(vinyl chloride) and found to be miscible up to at least 50 wt%[19].

More recently, Paul, Barlow and coworkers have investigated two other systems involving, in both cases, poly(carbonate) (PC). In the first one[20], a polyester is used to solubilize PC and a poly(styrene-*co*-acrylonitrile) (SAN) containing 25 wt% acrylonitrile. With poly(caprolactone) (PCL), they found miscibility at PCL concentrations larger than 29%, whatever the PC/SAN ratio. With poly(1,4-butylene adipate) (PBA) and poly(1,4-cyclohexane dimethylenesuccinate) (PCDS) instead of PCL, miscibility was in general found except at very low PBA and PCDS concentrations (a few per cent). These latter polyesters, and particularly PCDS, are then very effective compatibilizing agents, surprisingly more

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effective than PCL. In the second system investigated[21], PCL is used to solubilize PC and phenoxy. Miscibility is found at PCL concentrations larger than 48 wt%. These two results obtained with PCL are consistent with the fact that the addition of up to 30 wt% diethyl phthalate has been unsuccessful in solubilizing poly(arylate) with cellulose acetate[22].

Finally, Belaribi *et al.*[23] have found that poly(tetramethyl carbonate) (MPC) has more affinity for PC than for poly(styrene) (PS) in ternary blends where binary PS/MPC blends are fully miscible whereas PC/MPC blends are miscible only up to 70 wt% PC. This observation is consistent with the asymmetry found by Paul, Barlow and coworkers in each of the ternary blends that they investigated[20,21]. It is certainly related to different affinities, or degrees of miscibility, between the different polymer pairs. This phenomenon has been observed on model compounds of polyester/chlorinated polymer blends to the extent that a scale of interaction could be established[24-26].

It can also be expressed by the determination of thermodynamic interaction parameters between pairs of blend components as done in refs. 20 and 21. This approach was in fact used before for ternary mixtures of a polymer and two solvents, or two polymers and one solvent[27].

In this article, T_g values obtained with ternary PCL/PVC/CPVC blends will be used to gain information on the relative miscibility of PVC and CPVC with PCL.

EXPERIMENTAL

The polymers used in this study and their main characteristics are given in *Table 1*. PCL, PVC and CPVC were supplied by Aldrich Chemicals, Shawinigan Chemicals and BF Goodrich, respectively. CPVC contains 67.2 wt% chlorine, with about twice as many CHCl groups as CH_2 groups, and with about 7% of CCl_2 groups[28].

Blends of PCL/PVC/CPVC were prepared by slowly casting films from tetrahydrofuran (THF) solutions containing adequate proportions of each homopolymer. Solvent evaporation was first conducted at room temperature; then, to ensure complete removal of THF, the films were dried for three weeks in a vacuum oven until they reached constant weight. Film thicknesses were about 45 μm. Films containing less than 60% PCL were transparent; the others were opaque because they contain crystalline PCL.

Differential scanning calorimetry (d.s.c.) measurements were conducted with a Perkin–Elmer DSC-4 apparatus equipped with a TADS microcomputer; the apparatus was calibrated with indium, which has a melting temperature of 429.6 K and an enthalpy of fusion of 28.5 J g^{-1}.

After its insertion in the d.s.c. apparatus, the sample was first cooled to 170 K for 20 min. A first scan was made

at a heating rate of 80 K min^{-1}, up to 435 K, where it stayed for 2 min. Then, it was quenched to 170 K at a cooling rate of 320 K min^{-1}. It was again left for 10 min at that temperature before a second scan at a heating rate of 40 K min^{-1}. The same thermal cycle was then repeated with a heating rate of 20 K min^{-1}. For several samples, the same cycle was repeated several times in order to verify the reproducibility of the results. The values of T_g reported in this paper were recorded during the third scan at a heating rate of 20 K min^{-1}, and were taken at the half-height of the heat capacity jump of the glass transition.

RESULTS

The d.s.c. curves of a large number of ternary PCL/PVC/CPVC blends were recorded. In a first step, we have tried to distinguish mixtures exhibiting only one T_g at a temperature different from those of the pure homopolymers, and those exhibiting two or three T_g values. (In the following section, a more detailed analysis of the data will be carried out.) *Figure 1* shows the sort of variation that can be detected for blends containing an equal amount of PVC and CPVC and the indicated amount of PCL. Blends containing 25, 30, 33 and 35% PCL clearly exhibit two T_g values, one close to that of pure CPVC ($T_g = 393$ K) and another one below that of pure PVC ($T_g = 354$ K); in addition, the latter T_g decreases with increase of the PCL content of the mixture whereas the former remains constant. However, a blend containing 37.5% PCL exhibits only one T_g. Therefore, we believe that it is possible to distinguish one-T_g blends from two-T_g mixtures, a significant difference being observed with a variation of a few per cent in their composition, at least in the most favourable cases[15].
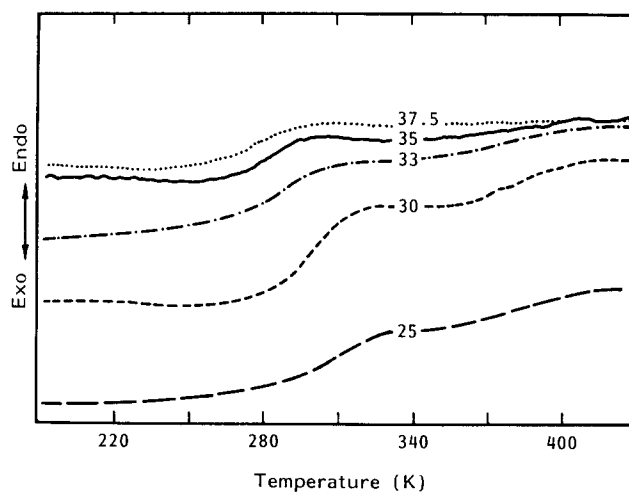

Figure 1 D.s.c. curves of PCL/PVC/CPVC blends having a PVC/CPVC ratio of 1.0. The number on each curve is the amount of PCL (wt%) in the mixture

Table 1 Polymers used

Polymer	Acronym	Repeat unit	T_g (K)	M_w (kg mol^{-1})	Supplier
Poly(caprolactone)	PCL	$\{(CH_2)_5-COO\}_n$	209	20	Aldrich
Poly(vinyl chloride)	PVC	$\{CH_2-CHCl\}_n$	354	80	Shawinigan
Chlorinated PVC	CPVC	–	393	100	BF Goodrich

From similar measurements, it is possible to establish the ternary diagram shown in *Figure 2*, where the full circles correspond to mixtures where a single T_g was observed and the open circles correspond to those where two or three T_g values were recorded. The full curve represents the boundary between the two regions. We notice immediately that this boundary is not symmetrical with respect to the PVC and CPVC apexes and that the PCL concentration range where one T_g is observed is broader at high CPVC/PVC ratios than it is at high PVC/CPVC ratios. We also notice, at high PVC/CPVC ratios, that two T_g values are recorded close to the side of the triangle, although the binary PCL/PVC mixtures are miscible and exhibit only one T_g as reported by several authors[5-7] and verified in this laboratory[15] with the same polymers that were used to prepare the ternary mixtures. This observation means that the solubility of the polymers is very limited at those PCL concentrations, at least at high PVC/CPVC ratios; at high CPVC/PVC ratios, the solubility range is slightly broader.

Figure 2 also contains a broken curve, which represents the boundary between amorphous and semicrystalline blends[15]: above this line, PCL is found to be semicrystalline when the sample is prepared from THF or from the melt; below this line, the mixture is completely amorphous, except close to the boundary where a limited amount of PCL crystals can be grown if the sample is annealed for several weeks. Blends containing 44% or more PCL usually show some crystallinity. It is fortuitous to find the crystallization boundary line tangential to the one-T_g/two-T_g boundary on the left-hand side of the diagram.

DISCUSSION AND CONCLUSIONS

Let us begin the analysis of the results by looking at the behaviour of binary blends. *Figure 3* shows data reported in the literature by Koleske and Lundberg[5], Robeson[6], Hubbell and Cooper[7], and our own work[15] for PCL/PVC

Figure 3 Glass transition temperature of binary PCL/PVC blends as a function of composition. Data from Koleske and Lundberg[5] (O), Robeson[6] (●), Hubbell and Cooper[7] (▲) and our work[15] (■)

blends. These data superpose well and they are represented (full curve of *Figure 3*) by the Fox equation[4]:

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

where W_i is the weight fraction of component i and T_{gi} is its glass transition temperature. For plotting equation (1), T_g values of 203 and 354 K were used for PCL and PVC, respectively. The PVC value agrees with that found in this study and reported in *Table 1*; but the PCL value is slightly below that reported in this study. It was, however, used in *Figure 3* in order to allow for a consistent comparison with the other data reported by the same authors. *Figure 3* then shows that the T_g-composition data of PCL/PVC blends can be well represented by the Fox equation.

Similarly, the T_g data of PCL/CPVC blends[8] are shown in *Figure 4* and analysed in terms of equation (1) using the T_g values of *Table 1*. The agreement is satisfactory, although there are more fluctuations than in the previous case. *Figure 4* then shows that the T_g-composition data of PCL/CPVC blends can be well represented by the Fox equation. In view of these observations, analysis of the T_g values of ternary blends that show a single T_g will be carried out using equation (1) as a reference point.

A typical example is shown in *Figure 5*, which corresponds to a ternary PCL/PVC/CPVC blend with a PVC/CPVC ratio of unity. At low PCL concentrations, one observes two T_g values: one close to that of pure
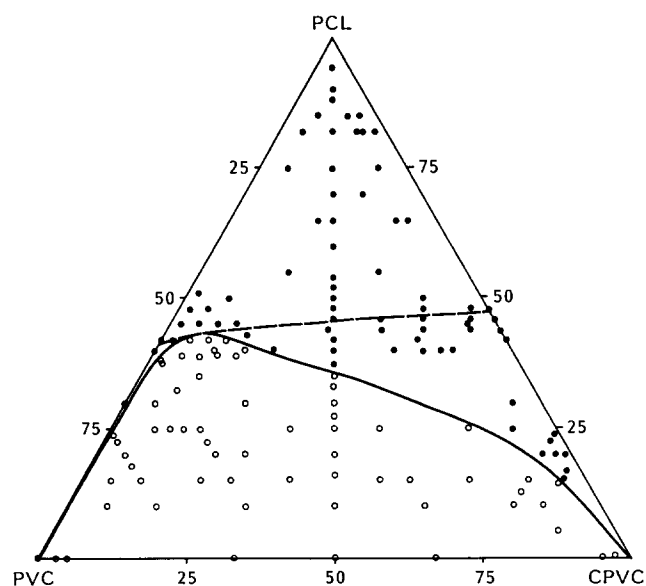
Figure 2 Ternary PCL/PVC/CPVC blend diagram. The full circles correspond to mixtures exhibiting one T_g and the open circles to those having several T_g values. The full curve is the boundary between the two regions. The broken curve is the boundary between amorphous and semicrystalline blends. See text for more details
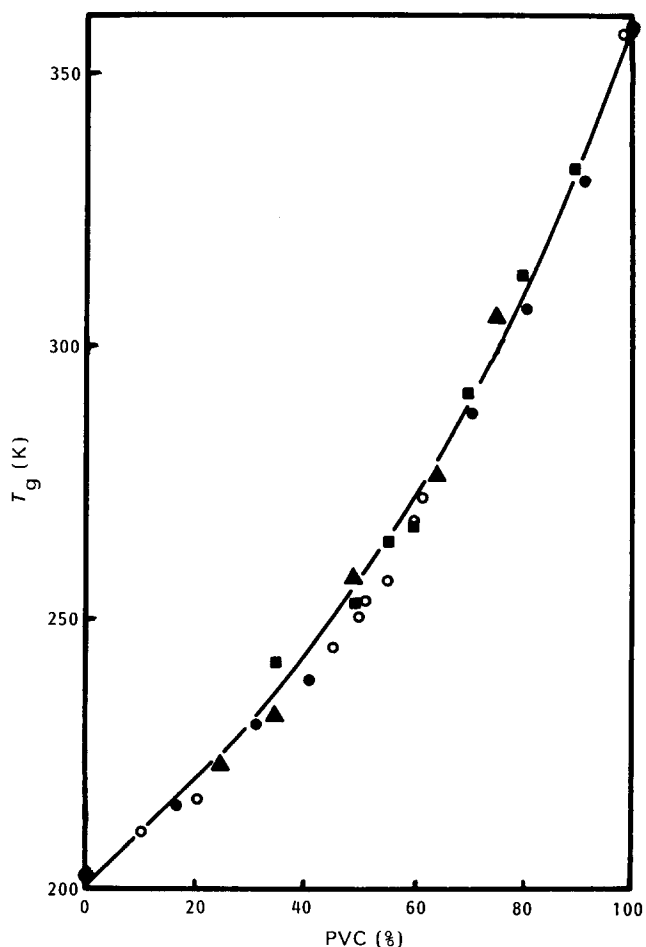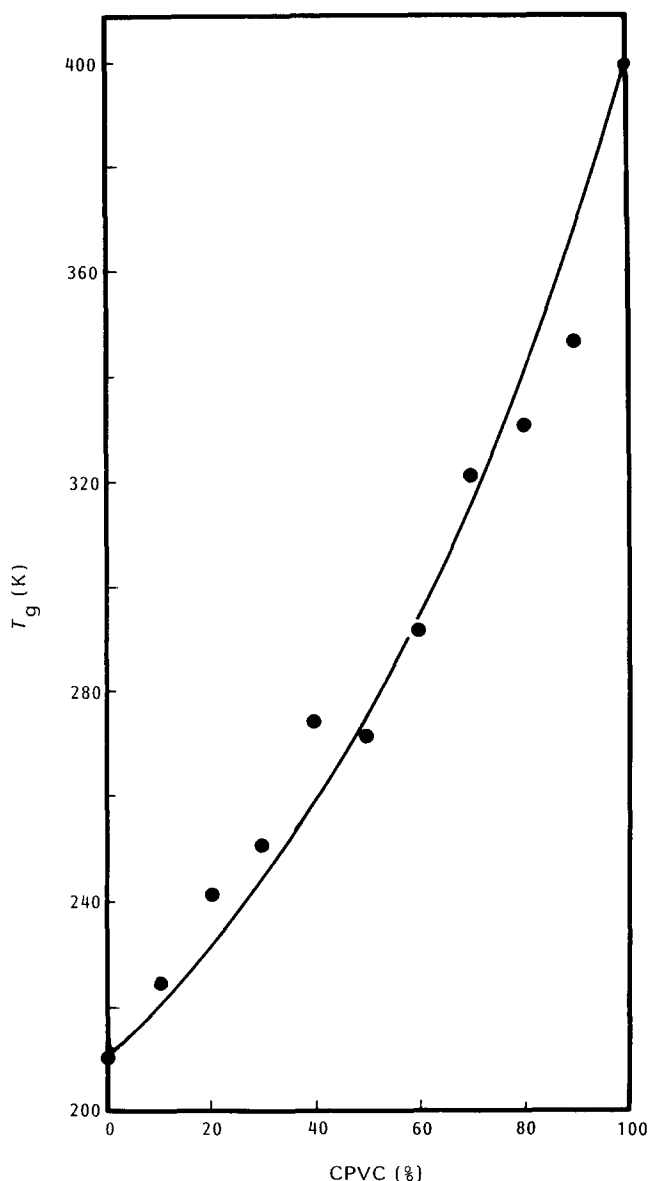
Figure 4 Glass transition temperature of binary PCL/CPVC blends as a function of composition. Data from ref. 8

CPVC, which does not shift with composition; and another one, which is composition-dependent. These dual values are observed up to PCL concentrations of 35%. Above this concentration, one observes only one T_g, which extrapolates, more or less, to that of pure PCL at 209 K.

These experimental values were analysed with the Fox equation using for the homopolymers the T_g values reported in *Table 1*. The bottom curve (A) of *Figure 5* is drawn assuming that a binary PCL/PVC blend is formed; the upper curve (B) assumes the presence of a binary PCL/CPVC blend; and the intermediate curve (C) is calculated for a ternary PCL/PVC/CPVC blend using:

$$T_g^{-1} = W_1/T_{g1} + W_2/T_{g2} + W_3/T_{g3} \qquad (2)$$

In the concentration range where a single T_g is recorded, it is seen that the difference between the three curves is smaller than the experimental accuracy of the measured parameter, which makes any attempt to distinguish between the formation of a single phase made up of the three polymers involved and the coexistence of two binary

PCL/PVC and PCL/CPVC phases impossible. The discrimination between these two possibilities would require the use of chlorinated homopolymers having very different values of T_g such that the curve corresponding to a true ternary mixture and those corresponding to coexisting binary phases would be apart by more than 15 K. Other workers had exactly the same problem with other ternary blends[18,20,21]. However, if coexisting PCL/PVC and PCL/CPVC phases are formed, PCL distributes itself almost equally between the two phases, which is the assumption made in calculating the two curves shown in *Figure 5*. Otherwise, important deviations between the experimental data and the calculated values would show up.

From a different point of view, the presence of a single T_g, intermediate between those of the pure components, is usually taken as evidence of miscibility between polymers[2,3], although it is generally recognized that the scale of measurement of T_g is of the order of 10 nm and that T_g is not, therefore, a molecular probe[29,30]. In the sort of ternary blends investigated herein, a single T_g indicates the solubility of PCL in PVC and CPVC because, otherwise, the T_g of at least one of the homopolymers would still be detected (except at extreme concentrations). However, as mentioned above, the miscibility of PCL can occur by the formation of a single ternary phase made up of the three polymers of the mixture, or by its miscibility in coexisting PVC and CPVC phases. These two different situations have been suggested by Shah et al.[20], at different concentrations, whereas Equiazabal et al.[22] have suggested the formation of coexisting phases between diethyl phthalate and two
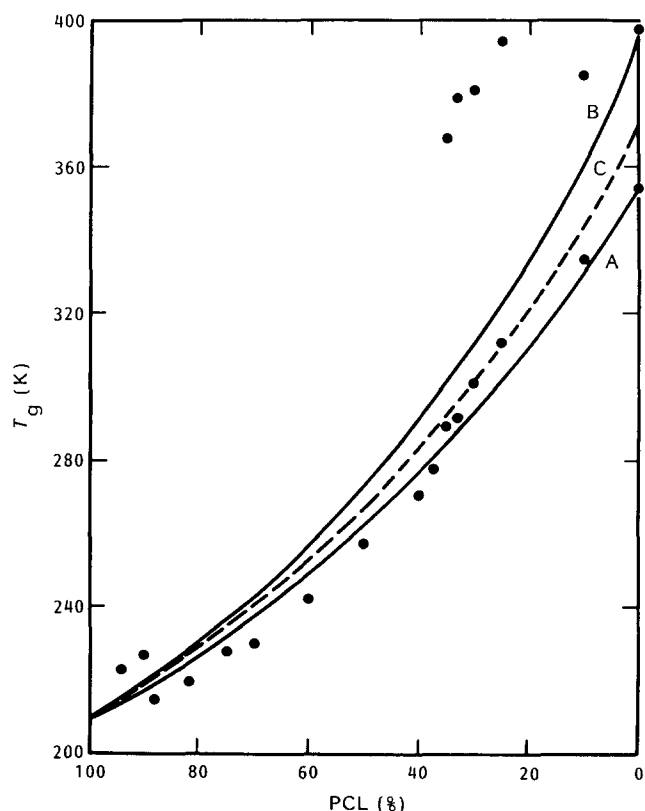

Figure 5 Glass transition temperature of ternary PCL/PVC/CPVC blends as a function of PCL composition for mixtures having a PVC/CPVC ratio of 1.0: curve A, binary PCL/PVC blend; curve B, binary PCL/CPVC blend; curve C, ternary PCL/PVC/CPVC blend. See text for more details

polymers at plasticizer concentrations smaller than 30%. Larger concentrations were not investigated by these authors.

In the area of *Figure 2* where several T_g values are detected, different situations can occur. First, there is a very limited zone where two T_g values are recorded close to those of the pure chlorinated polymers (the T_g of PCL was not seen owing to its very small concentration in this range); this situation is only found at very small PCL concentrations and at PVC/CPVC ratios close to unity.

Secondly, at PVC/CPVC ratios equal to or smaller than unity, one sees a T_g close to that of pure CPVC and a second one that is composition-dependent (*Figures 1* and *5*). These observations indicate the presence of a separate CPVC phase containing little or no PCL and a second phase where PCL plastifies PVC and/or CPVC. This is the dominant zone of the bottom part of the ternary diagram. In that zone, the presence of a third PCL phase, whose T_g would be undetected due to its low concentration and low intensity, is not excluded.

Thirdly, at PVC/CPVC ratios larger than unity, one observes two T_g values: one below 393 K, and another below 354 K; both are composition-dependent for a constant PVC/CPVC ratio. One can reasonably assume that this zone corresponds to the formation of two coexisting PCL/PVC and PCL/CPVC phases with PCL distributed almost equally in the two phases.

The asymmetry of the ternary diagram (*Figure 2*), and the broader concentration range where a single T_g is observed at high CPVC/PVC ratios, could support an earlier suggestion[8,13] that PCL is more miscible with CPVC than with PVC because the former polymer contains a higher chlorine concentration and more interacting groups with PCL. This asymmetry certainly indicates different interaction parameters between the PCL/PVC and the PCL/CPVC pairs.

It can be modelled assuming that the heat of mixing ΔH_m of a ternary system can be described in terms of binary interaction coefficients by:

$$\Delta H_m = 2RT(\chi_{12}\phi_1\phi_2 + \chi_{13}\phi_1\phi_3 + \chi_{23}\phi_2\phi_3) \quad (3)$$

where R is the gas constant, T the temperature, χ_{ij} the thermodynamic interaction parameter (which determines the sign and magnitude of the heat of mixing of i with j) and ϕ_i is the volume fraction of component i in the mixture. Equation (3) assumes that the χ parameters are independent of concentration and symmetrical, i.e. $\chi_{ij} = \chi_{ji}$. For the purpose of the present discussion, equation (3) can be reduced, for measurements carried out at a constant temperature, to:

$$\chi \approx \chi_{12}\phi_1\phi_2 + \chi_{13}\phi_1\phi_3 + \chi_{23}\phi_2\phi_3 \quad (4)$$

where χ is the thermodynamic interaction parameter of the ternary blend.

Equation (4) was then used to calculate the miscibility/immiscibility boundary observed in *Figure 2*. For that purpose, immiscibility was associated with a positive value of χ and miscibility with a negative value. Concentrations were then calculated where χ is equal to zero, assuming that a true ternary solution is present in the area where a single T_g is observed. Calculations were carried out using a χ_{12} value between PCL and PVC of -0.3; this is the average χ value determined in ref. 14. The value of χ_{13}, between PCL and CPVC, was selected as
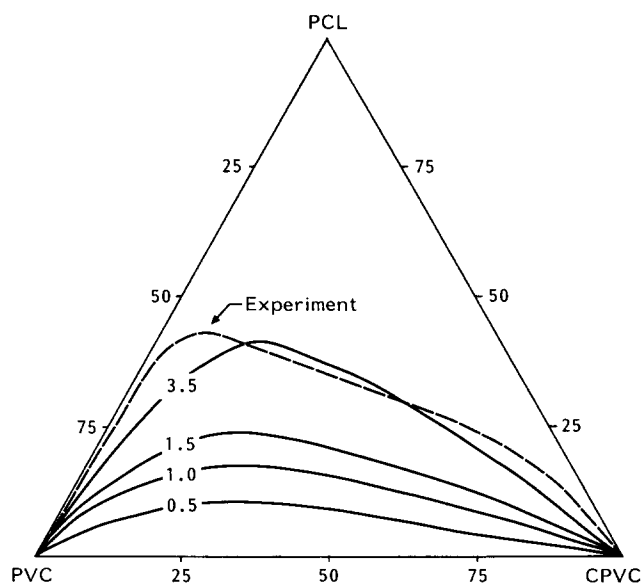

Figure 6 Ternary PCL/PVC/CPVC blend diagram. Calculations were made with equation (4) and with $\chi_{12} = -0.3$ and $\chi_{13} = -1.8$. The number on each curve is the value of χ_{23} used in the calculation

being more negative than χ_{12}; this is a necessary requirement in order to induce an asymmetry in the boundary curve such as that shown in *Figure 2*. Finally, χ_{23}, between PVC and CPVC, was selected as being positive because of the immiscibility between these two homopolymers.

As shown in *Figure 6*, reasonable agreement is found between the experimental curve and the curve calculated with a value of $\chi_{13} = -1.8$ and a value of $\chi_{23} = 3.5$. Smaller χ_{23} values significantly decrease the boundary line and are not satisfactory. Smaller χ_{13} values decrease the asymmetry of the calculated line and are not acceptable. The present approach, with its numerous assumptions and imperfect agreement with the experimental data, cannot be interpreted in a fully quantitative manner. Nevertheless, it certainly indicates stronger PCL/CPVC than PCL/PVC interactions, and strong repulsions between PVC and CPVC.

In summary, a single T_g is observed in ternary PCL/PVC/CPVC mixtures containing 40% or more PCL. However, we do not believe that this observation necessarily indicates the presence of a homogeneous ternary PCL/PVC/CPVC phase; it could equally well be explained by the coexistence of two binary PCL/PVC and PCL/CPVC phases. The accuracy of the T_g measurements does not allow us, with this particular system, to distinguish between these two possibilities because the T_g values of PVC and CPVC are too close to one another.

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