Miscibility in PVC-polyester blends

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Blends of poly(vinyl chloride), PVC, with the polyesters poly(butylene adipate), poly(hexamethylene sebacate), poly(2,2-dimethyl,1,3-propylene succinate) and poly(1,4-cyclohexanedimethanol succinate) were found to exhibit a single, composition dependent glass transition. Thus, these polyesters are miscible with PVC as others have reported for poly(ε-caprolactone). However, mixtures of poly(ethylene succinate), poly(ethylene adipate) and poly(ethylene *ortho*phthalate) with PVC were found not to be miscible. Melting point depression has been used to estimate the blend interaction parameter. These results combined with others from the literature suggest that there is an optimum density of ester groups in the polymer chain for achieving maximum interaction with PVC. Too few or too many ester groups result in immiscibility with PVC.

INTRODUCTION

Commercial products based on poly(vinyl chloride), PVC, frequently are blends with other polymers for the purpose of achieving improved impact strength[1] or permanent plasticization[2]. As a result, there has been considerable interest in the thermodynamic miscibility of PVC with other polymers[3,4]. Many of the polymers which have been found to be miscible with PVC contain carbonyl groups[3], and one of the most widely studied examples is poly(ε-caprolactone), PCL[5-7]. Recent results have shown that the thermodynamic basis for this miscibility is a specific interaction between the carbonyl oxygen and the PVC molecule[8,9] which can lead to a net exothermic heat of mixing.

This knowledge suggests that PVC ought to be miscible with a wider range of polyesters than just PCL. In line with this, more recent publications have revealed PVC to be miscible with some other polylactones from the β-propiolactone series[10] and with poly(butylene terephthalate)[11] (see *Table 1*). The purpose of this paper is to explore further the range of polyesters which are miscible with PVC and to obtain better insight into the relationship between molecular structure of the polyester and miscibility with PVC.

MATERIALS AND PROCEDURES

All of the polyesters used in this study and listed in *Table 2* are speciality polymers purchased from the Aldrich Chemical Co. except for PCL. No molecular weight information is available for these polymers, but this knowledge is not critical since we feel that the state of miscibility in the present blends is primarily influenced by the heat of mixing between the two polymers with entropic effects being much less important[4]. The PCL was obtained from the Union Carbide Corp. through the courtesy of Dr. L. M. Robeson and is a commercial product designated as PCL-700. It was incorporated in this study basically as a control since much information about its blends with PVC is available in the literature. The PVC was also obtained from the Union Carbide Corp. and is a commercial product, designated as QYSJ-5, made by a suspension process for fabrication applications.

Blends of the various polyesters with PVC were prepared in solution using tetrahydrofuran as the solvent. In some cases, it was necessary to employ elevated temperatures to dissolve the semi-crystalline polyesters. Final solvent removal was accomplished in a vacuum oven at 100°C for 24 h. When the blends were to be exposed to higher temperatures, a stabilizer, Vanstay 6053, was added.

Thermal analysis was performed using an R. L. Stone DTA with the sample under a nitrogen environment. In all instances, the heating rate was 10°C min^{-1}; whereas, cooling was at 40°C min^{-1}. After loading, each sample was heated to 100°C and held there for 20 min. Following the return to room temperature, several cycles up to 10°C above the highest transition and down to 50°C below the lowest transition were made with thermograms being traced while heating only.

GLASS TRANSITION BEHAVIOUR

The appearance of a single, composition dependent glass transition, T_g, is used as a criterion for blend miscibility. The glass transitions observed for each pure polymer employed here agreed well with those reported by other investigators[13]. Each T_g recorded was the average value for several heats, and a range is shown where identical values were not observed.

Poly(ε-caprolactone)

Figure 1 shows the glass transition behaviour of PCL–PVC blends observed in this study along with the earlier results from Koleske and Lundberg[5]. The agreement between the two sets of data is satisfactory, which lends confidence in subsequent results for systems not previously studied. Based on these and many other observations, it is evident that PVC–PCL is a miscible system.

Poly(1, 4-butylene adipate)

Figure 2 demonstrates a single composition dependent glass transition for blends of PBA with PVC and leads to

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Table 1 Summary of previous literature on PVC–polyester miscibility

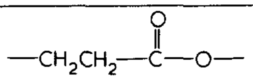
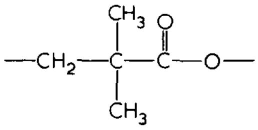
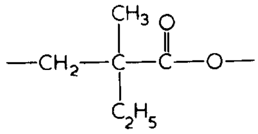
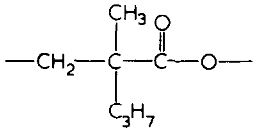
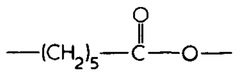
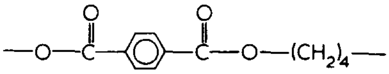
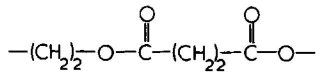
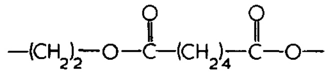
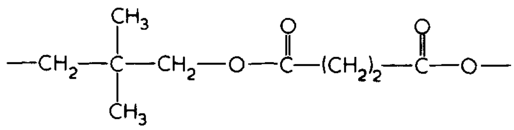
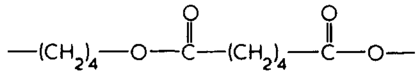
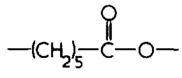
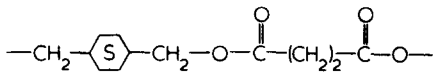
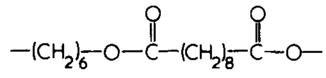
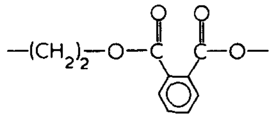
Polyester	Abbreviation	Structure	Comments	Reference
Poly(β-propiolactone)	BPL	 $-CH_2CH_2-\overset{\overset{O}{\|}}{C}-O-$	Not miscible	12
Poly(pivalolactone)	PPL	 $-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\overset{O}{\|}}{C}-O-$	T_g too close to that of PVC to use this criterion, but less direct evidence suggests miscibility	10
Poly(α-methyl-α-ethyl-β-propiolactone	MEPL	 $-CH_2-\underset{C_2H_5}{\overset{CH_3}{C}}-\overset{\overset{O}{\|}}{C}-O-$	Miscible	10
Poly(α-methyl-α-n-propyl-β-propiolactone	MPPL	 $-CH_2-\underset{C_3H_7}{\overset{CH_3}{C}}-\overset{\overset{O}{\|}}{C}-O-$	Miscible	10
Poly(ϵ-caprolactone)	PCL	 $-(CH_2)_5-\overset{\overset{O}{\|}}{C}-O-$	Miscible	5
Poly(butylene terephthalate)	PBT		Miscible	11

Table 2 Polyesters used in current study and a summary of their miscibility with PVC

Polyester	Abbreviation	Structure	Comments
Poly(ethylene succinate)	PES	 $-(CH_2)_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_2-\overset{\overset{O}{\|}}{C}-O-$	Not miscible
Poly(ethylene adipate)	PEA	 $-(CH_2)_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-O-$	Not miscible
Poly(2,2-dimethyl-1, 3-propylene succinate)	PDPS	 $-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_2-\overset{\overset{O}{\|}}{C}-O-$	Miscible
Poly(butylene adipate)	PBA	 $-(CH_2)_4-O-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-O-$	Miscible
Poly(ϵ-caprolactone)	PCL	 $-(CH_2)_5-\overset{\overset{O}{\|}}{C}-O-$	Miscible
Poly(1,4-cyclohexanedimethanal succinate)	PCDS		Miscible
Poly(hexamethylene sebacate)	PHS	 $-(CH_2)_6-O-\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}-O-$	Miscible
Poly(ethylene orthophthalate)	PEOP		Not miscible

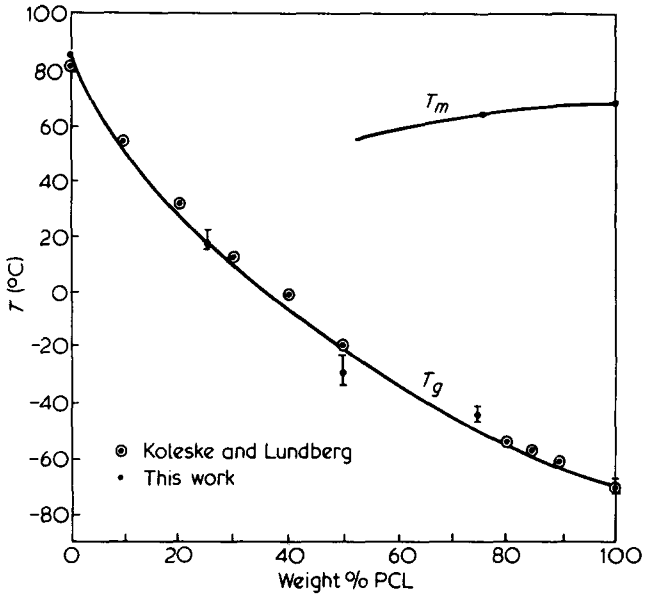


Figure 1 Transitions for PCL–PVC blends

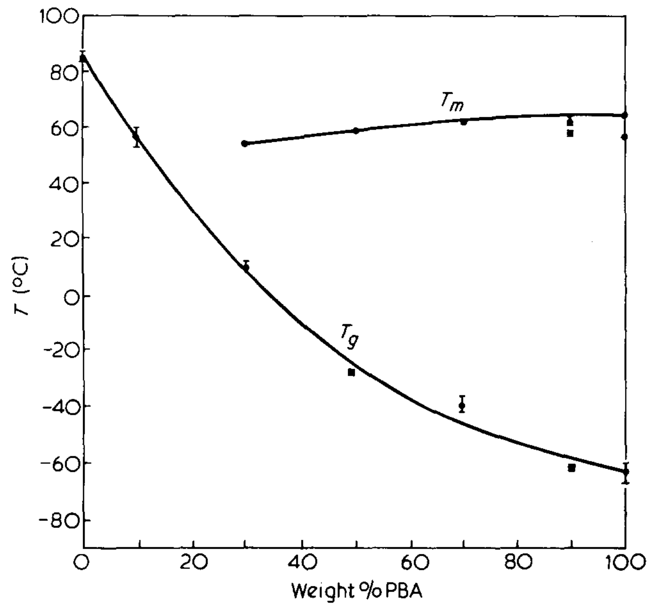


Figure 2 Transitions for PBA–PVC blends

the conclusion that this pair of polymers is miscible as well. Like PCL, this polyester crystallizes from the blend, and the observed melting point is shown. More will be said about this later.

Poly(2, 2-dimethyl-1, 3-propylene succinate)

PDPS did not crystallize in the pure form or when blended with PVC. The glass transition behaviour of its blends with PVC is shown in *Figure 3* which clearly establishes this as a miscible system.

Poly(1, 4-cyclohexanedimethanol succinate)

The single, composition dependent glass transition for PCDS–PVC blends shown in *Figure 4* leads to the conclusion that this system also is miscible.

Poly(hexamethylene sebacate)

Blends of PHS with PVC also exhibit a single, composition dependent glass transition, as shown in *Figure 5*, which demonstrates this pair to be miscible.

Poly(ethylene adipate)

All of the previously mentioned blends were reasonably tough after films were cast from THF; however, PEA–PVC blends were very brittle and cracked during handling. The specimens were quite opaque at room temperature and did not become clear above the T_m of PEA. Some

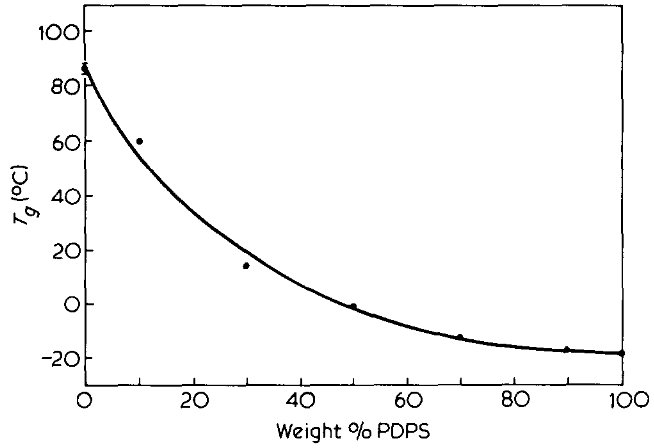


Figure 3 Glass transition behaviour of PDPS–PVC blends

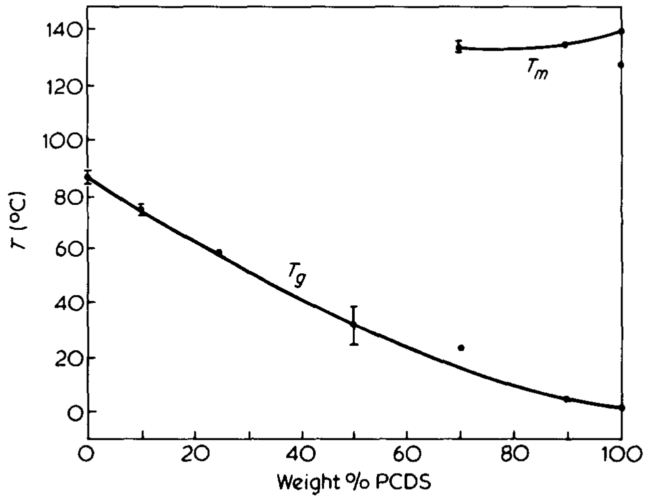


Figure 4 Transitions for blends of PCDS and PVC

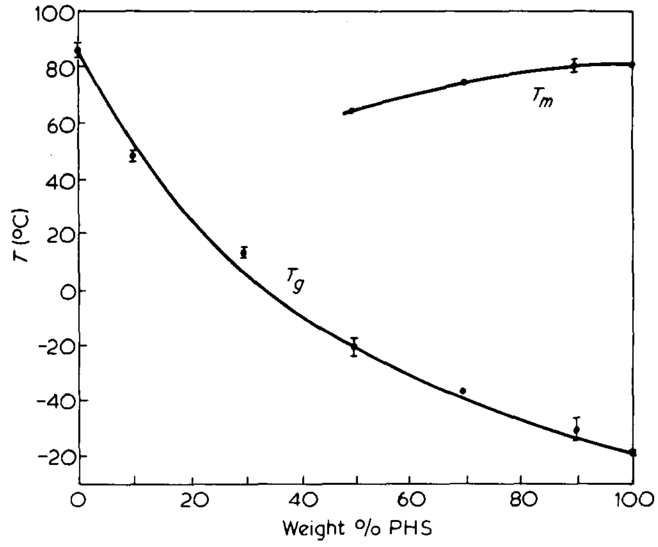


Figure 5 Transition behaviour of PHS–PVC blends

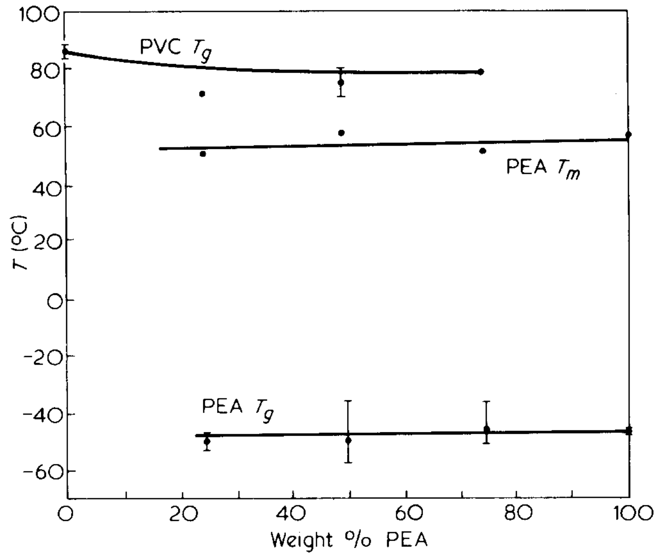


Figure 6 Transition behaviour for mixtures of PEA and PVC

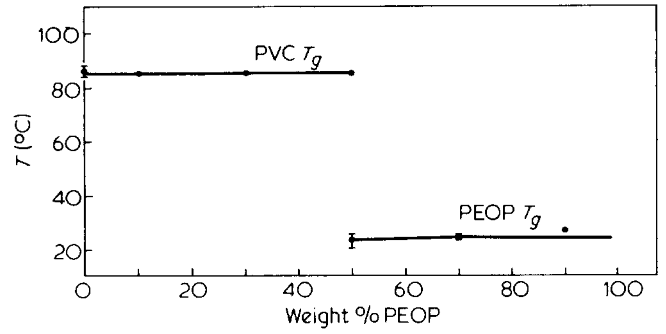


Figure 7 Glass transition behaviour of PEOP—PVC mixtures

of the previously mentioned blends exhibited opacity or haze at low temperatures, owing to polyester crystallinity, but all became fully transparent above T_m. *Figure 6* shows the transition behaviour observed for these blends by d.t.a. At all compositions examined, glass transitions for each component are evident with only minor shifts in temperature locations. The T_m for PEA lies between the T_g's of the two components. Crystallization seemed to occur unaffected by the presence of PVC. It is quite evident that this pair are not miscible.

Poly(ethylene ortho*phthlate)*

THF cast films of PEOP–PVC mixtures were opaque and brittle despite the fact that the PEOP did not crystallize. These films did not become transparent on heating to any temperature. *Figure 7* shows the glass transition behaviour noted for these blends by d.t.a. Addition of either polymer to the other did not significantly alter the T_g from that observed for the pure component. For some reason, it was very difficult to detect a significant baseline shift at the T_g of the minor component even though the T_g of the major component was not shifted from that of the pure polymer. Based on all evidence, we conclude this pair not to be miscible.

Poly(ethylene succinate)

PES is not appreciably soluble in THF, and no fully satisfactory mutual solvent for it and PVC was found. However, repeated attempts to combine these two polymers using mixed solvents, partial solvents, etc. led us to the conclusion that PES and PVC are not miscible.

CRYSTALLIZATION AND MELTING BEHAVIOUR

All of the polyesters listed in *Table 2* crystallized during the thermal analysis except PDPS and PEOP. Kinetic considerations affect crystallization from miscible blends as reviewed previously^{15} with the difference between the melting point of the crystallizable component and the glass transition of the blend being the main governing parameter. For the present blends, crystallization occurred during cooling in some cases and upon heating in others for the cyclic heating and cooling scheme described earlier. *Figure 8* shows the area under the melting endotherm recroded during heating for the crystallizable polyesters found to be miscible with PVC. In each case, the endotherm area (based on total sample mass) became zero at a finite content of polyester in the blend, illustrating the kinetic effect on crystallization rate described earlier^{15,16}.

Melting point depression analysis for a crystallizable component in a miscible blend can be used to estimate the interaction parameter, χ_{12} or B, between components^{16,17}. Using the Flory–Huggins theory for mixtures, the melting point depression can be divided into enthalpic and entropic contributions^{16}, but the latter are negligible, provided the molecular weights of both components are adequately large, as assumed here. The remaining enthalpic part is given by

$$\Delta T_m = -T_{m2}(V_u/\Delta H_u)_2 B \varphi_1^2 \qquad (1)$$

where component 2 is the crystallizable component, T_{m2} is

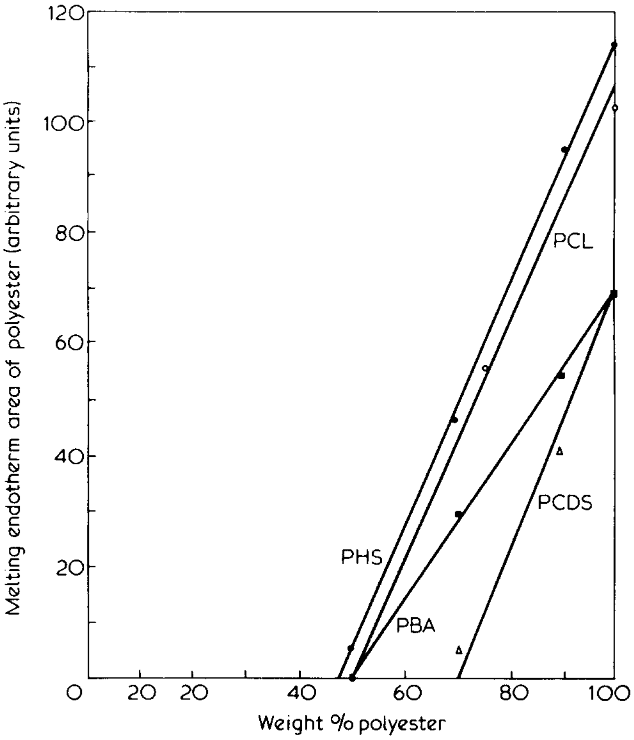


Figure 8 Polyester endotherm area (based on total sample mass) for miscible blends with PVC. Area was recorded on heating during cyclic heating at 10°C min^{-1} and cooling at 40°C min^{-1} in the d.t.a.

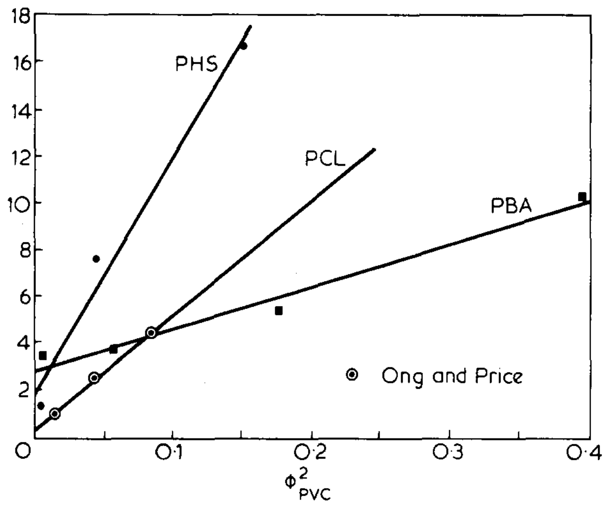


Figure 9 Melting point depression plots for various polyesters with PVC

its melting point in the pure state, $(\Delta H_u/V_u)_2$ is its heat of fusion per unit volume, and φ_1 is the volume fraction of the amorphous component. The parameter B is related in principle to the heat of mixing through

$$\Delta H_{mix} = B\varphi_1\varphi_2 \qquad (2)$$

although B, in practice, is a free energy parameter related to the more familiar interaction parameter by

$$\chi_{12} = \frac{BV_1}{RT_{m2}} \qquad (3)$$

For the present discussion, V_1 will be taken as the molar volume of a PVC repeat unit, 44.3 cm^3 mol^{-1}.

The melting point data shown here are rather sparse since the collection of such data was not part of the primary objective of this study. Furthermore, it has been suggested that such data ought to be determined under conditions that control crystal size since this can affect the observed melting point[18]. Nevertheless, an analysis of the current data does prove interesting, but the results must be regarded as tentative until a more thorough experimental program has been executed. *Figure 9* shows the observed melting point depression *versus* the square of the PVC volume fraction as suggested by equation (1). Reasonably good, straight lines are seen, but as observed in many other instances[15–17], there is a small positive intercept on the ΔT_m axis. The data of Ong and Price[7] for PCL are also included here. Data for PCDS-containing blends are not shown because of the complex melting behaviour observed for this system. No results of this type are possible for PDPS blends since this polyester does not crystallize.

Slopes of these lines were computed and converted into χ_{12} values via equations (1) and (3) using published values of $(\Delta H_u/V_u)$. However, data for the latter quantity were not available for PBA so an estimate based on values for other polyesters was made. The interaction parameters so determined are shown in *Figure 10*, and their possible significance will be discussed later.

VISUAL OBSERVATIONS

At room temperature, blends of PVC with PDPS were clear since this polyester is miscible with PVC and does not crystallize. However, PCL, PBA, PCDS and PHS were not similarly clear because of crystallinity; but each blend did become clear upon heating above the melting point of the polyester component. To the contrary, blends containing PEA, PES and PEOP which were judged immiscible with PVC were not clear at any temperature.

Many miscible blends have been reported to exhibit lower critical solution temperature, *LCST*, behaviour at elevated temperatures[19]. Using procedures described earlier[19,20], all miscible blends reported here were heated to the PVC decomposition temperature (250°–300°C with rapid heating for stabilized blends), but no evidence for *LCST* behaviour was found.

DISCUSSION

Based on the appearance of a single glass transition temperature, these studies show that the polyesters PBA, PDPS, PCDS and PHS form miscible blends with PVC; whereas PEA, PES and PEOP do not. Thus, it is concluded that the miscibility of the polyester PCL with PVC is not unique.

Since the basis for miscibility of polyesters with PVC is a specific interaction involving the carbonyl oxygen, it is somewhat surprising that immiscibility was found for those polyesters having the highest density of carbonyl groups, i.e. PES and PEA. However, this is in line with the findings of Coleman and Varnell[12] who noted that poly(β-propiolactone) is not miscible with PVC. Unlike these authors, we do not believe that simple arguments based on solubility parameter considerations are the explanation for this. A useful way to summarize the trends of aliphatic polyester miscibility with PVC is shown in *Figure 10*, where polymer–polymer interaction parameters estimated from melting point depression are plotted *versus* a measure of the proportion of ester

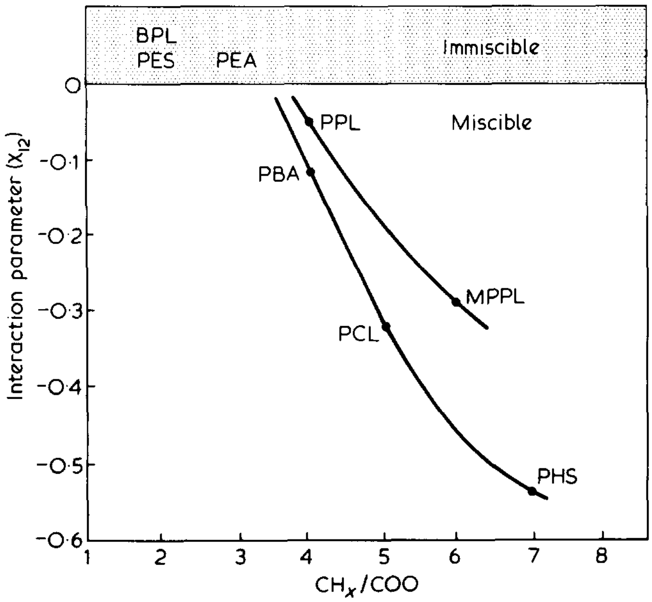


Figure 10 Blend interaction parameters estimated from melting point depression as a function of the number of aliphatic carbons per ester linkage in the polyester structure. Observations for MPPL and PPL were taken from Aubin and Prud'homme[10] while that for BPL is from Coleman and Varnell[12]

linkages in the polyester structure. The symbol CH_x denotes aliphatic carbon atoms in the repeat unit where x may have values of 0, 1, 2 or 3, depending on the substitution. In this diagram, PAS, PEA and BPL are located in the region $\chi_{12} > 0$ because they are known to be immiscible with PVC. The linear aliphatic polyesters form a curve in which χ_{12} becomes more negative as CH_x/COO increases while the branched aliphatic polyesters[10] form an analogous curve which is displaced upward slightly. Simple extrapolation of either curve to small ratios of CH_x/COO leads to the conclusion that χ_{12} will become positive for CH_x/COO values of 3 or less and that such polyesters would, therefore, be immiscible with PVC. This is exactly what was observed in the cases of PES, PEA and BPL. Clearly, the trends seen in *Figure 10* must reverse at some point since χ_{12} must become positive again at large values of CH_x/COO (polyethylene is not miscible with PVC). An interesting comparison can be made here with polymeric plasticizers based on copolymers of ethylene and carbon monoxide. Those containing 14 wt. % CO are not miscible with PVC while those containing 15 wt. % CO or more are miscible[2]. This suggests that χ_{12} should become positive again at a ratio of CH_2/COO of about 12 or more. Obviously, it would be of interest to explore the behaviour of χ_{12} at larger CH_x/COO ratios to better define this optimum range and to understand its mechanistic origin.

It is not surprising that the value of χ_{12} is more negative for linear polyesters compared to branched ones at the same value of CH_x/COO because of shielding or other issues that might affect the carbonyl–PVC interaction. Similar studies on the miscibility of polyesters with polycarbonate show that similar branching preclude miscibility for these reasons[21,22].

It is important to point out that the interaction parameters employed in *Figure 10* are only approximate values and that these trends should be regarded as tentative until more precise and complete studies have been completed.

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