Binary blends of poly(chloromethyl methacrylate) and poly(2-chloroethyl methacrylate) with some aliphatic polyesters

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(Received 13 August 1991; revised 15 October 1991; accepted 28 October 1991)

The miscibility behaviour of poly(chloromethyl methacrylate) (PCMMA) and poly(2-chloroethyl methacrylate) (PCEMA) with various aliphatic polyesters was studied by differential scanning calorimetry. PCMMA and PCEMA are miscible with poly(ethylene adipate), poly(butylene adipate), poly(hexamethylene sebacate) (PHS), poly(2,2-dimethyl-1,3-propylene succinate) and poly(2,2-dimethyl-1,3-propylene adipate). In addition, PCMMA is miscible with poly(ethylene succinate) whereas PCEMA is not. Blends of PCEMA with poly(2,2-dimethyl-1,3-propylene sebacate) exhibit upper critical solution temperature behaviour. Interaction parameters for PCMMA/PHS and PCEMA/PHS blends were evaluated from melting point depression analysis.

(**Keywords: miscibility; polymer blends; poly(chloromethyl methacrylate); poly(2-chloroethyl methacrylate); polyesters**)

INTRODUCTION

The miscibility behaviour of poly(ε-caprolactone) (PCL) with various chlorinated polymers has been widely reported. PCL is miscible with poly(vinyl chloride) (PVC)[1], chlorinated poly(vinyl chloride) (CPVC)[2], chlorinated polyethylene with chlorine contents greater than 30%[3], copolymers of vinylidene chloride (Saran)[4–6], polyepichlorohydrin[7], chlorinated polypropylene[8] and polychlorostyrene[8]. We have recently reported that PCL is miscible with poly(chloromethyl methacrylate) (PCMMA) and poly(2-chloroethyl methacrylate) (PCEMA)[9]. We have observed that in many respects, the miscibility behaviour of PCMMA and PCEMA is similar to that of PVC in forming miscible blends with several polymethacrylates[10,11], poly(*N*-vinyl-2-pyrrolidone)[12] and PCL[9].

The miscibility of PVC with PCL is attributed to hydrogen bonding interaction which has been confirmed by Fourier transform infra-red spectroscopic studies[13,14]. Ths miscibility of PCL with Saran has been attributed to hydrogen bonding interactions between the carbonyl groups and the β-hydrogens of Saran, and/or dipole–dipole interactions between the C–Cl and C=O groups[5,15]. For blends of PCMMA and PCEMA with PCL, the interactions are likely to involve the carbonyl groups of PCL and the hydrogens of the chloromethyl groups of PCMMA and PCEMA[9].

It has been shown that there is an optimum density of ester groups in the polyester chain for achieving maximum interaction with the chlorinated polymers. Ziska *et al.*[16] found that polyesters having CH_2/COO ratios less than 4 are immiscible with PVC whereas those having ratios of 4 or more are miscible with PVC at all observable temperatures. Woo *et al.*[17] confirmed Ziska's results and in addition found that miscibility results up to a CH_2/COO ratio of 10, where lower critical solution temperature (*LCST*) behaviour occurs, with the temperature of phase separation gradually decreasing as the CH_2/COO ratio becomes larger. Belorgey *et al.*[2] showed that CPVC is miscible with polyesters having CH_2/COO ratios of more than 3. Similar studies with Saran again demonstrated that an optimum value of CH_2/COO ratio is required to attain miscibility between a polyester and Saran[5,6]. In this paper we report the miscibility of PCMMA and PCEMA with various aliphatic polyesters.

EXPERIMENTAL

PCMMA and PCEMA were prepared by free radical polymerization as described previously[10,11]. The number-average molecular weight of PCMMA was 58 000 g mol^{-1} from intrinsic viscosity measurements using the appropriate Mark–Houwink equation[18]. The number-average and weight-average molecular weights of PCEMA, determined by g.p.c., were 40 000 and 65 000 g mol^{-1}, respectively. The characteristics of various polyesters used in this study are shown in *Table 1*.

All the blends were prepared by solution casting from tetrahydrofuran. The solvent was allowed to evaporate slowly at room temperature. The blends were then dried *in vacuo* at 70°C for 1 week.

The glass transition temperatures (T_gs) of various samples were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C min^{-1}. The T_g value was taken as the initial onset of the change of slope in the d.s.c. curve.

The blends were examined for the existence of *LCST* behaviour using the method described previously[10].

The melting points of some samples were also determined using the Perkin-Elmer DSC-4 differential

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0032-3861/92/153203-07

Table 1 Characteristics of polyesters

Polyester	Abbreviation	Source[a]	T_g (°C)	T_m (°C)	Molecular weight ($g\ mol^{-1}$)
Poly(ethylene succinate)	PES	SPP	−16	100	–
Poly(ethylene adipate)	PEA	SPP	−55	46	–
Poly(butylene adipate)	PBA	PS	−70	49	–
Poly(2,2-dimethyl-1,3-propylene succinate)	PDPS	SPP	−18	75	16000
Poly(2,2-dimethyl-1,3-propylene adipate)	PDPA	RPC	−60	40	–
Poly(2,2-dimethyl-1,3-propylene sebacate)	PDPSb	Aldrich	−60	11	–
Poly(hexamethylene sebacate)	PHS	SPP	−70	74	62000

[a] SPP = Scientific Polymer Products, Inc.; PS = Polysciences, Inc.; RPC = Ruco Polymer Corporation

scanning calorimeter. Each sample was heated to 100°C and kept at that temperature for 10 min. The sample was then cooled to the desired crystallization temperature where it was kept for 24 h. It was then scanned at 5°C min^{-1} to obtain the melting temperature (T_m) which was taken as the peak temperature of the melting endotherm.

RESULTS AND DISCUSSION

Poly(ethylene succinate) blends

All the blends were cloudy. However, PCMMA/PES blends turned clear upon heating above the melting point of PES, whereas PCEMA/PES blends remained cloudy. The cloudiness of PCMMA/PES blends arises from the crystallinity of PES and that of PCEMA/PES blends arises from PES crystallites and also the immiscibility of the blends. D.s.c. measurements revealed a single T_g for each of the PCMMA/PES blends; the T_g *versus* composition curve is shown in *Figure 1*. However, for PCEMA/PES blends, a glass transition at −16°C, corresponding to the T_g of PES, was observed regardless of the composition. The glass transition of PCEMA in the blend could not be observed as it was obscured by the crystallization peak of PES. The results show that PES is miscible with PCMMA but not with PCEMA. In comparison, other chlorinated polymers like PVC[16], CPVC[2] and Saran[5,6] are immiscible with PES.

Poly(ethylene adipate) blends

Blends containing 90 and 75 wt% PCMMA were clear but the rest of the PCMMA/PEA blends were cloudy. A PEA/PCEMA blend containing 90 wt% PCEMA was clear and the other blends were cloudy. The cloudiness disappeared upon heating above the melting point of PEA. D.s.c. measurements also revealed the existence of one T_g in each blend, showing that PEA is miscible with PCMMA and PCEMA. The two T_g *versus* composition curves are shown in *Figures 2a* and *2b*. In contrast, PVC[16,17], CPVC[2] and Saran[5,6] are immiscible with PEA. *LCST* behaviour was not observed for the two blend systems up to 300°C, the highest temperature attained by the apparatus.

Poly(butylene adipate) blends

The blends were cloudy but they turned clear upon heating above the melting point of PBA. The existence of a single T_g in each blend further confirms that PBA is miscible with PCMMA and PCEMA. The T_g *versus* composition curves are shown in *Figures 2c* and *2d*. *LCST* behaviour was not observed for the two blend systems.

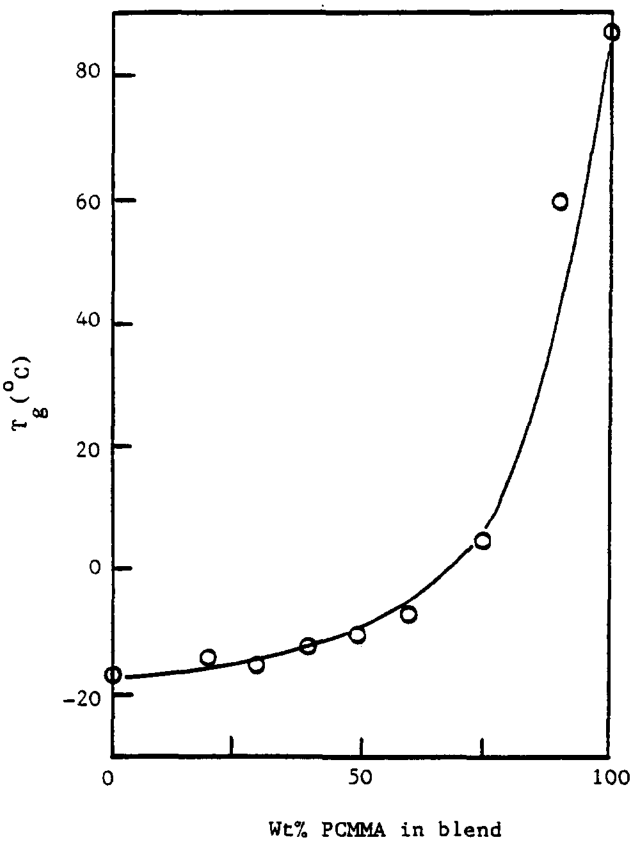

Figure 1 T_g *versus* composition curve for PCMMA/PES blend

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

Blends rich in PDPS were cloudy but they turned clear on heating above the melting point of PDPS. Each of the blends showed a single composition-dependent T_g; the T_g *versus* composition curves are shown in *Figures 3a* and *3b*. The blends did not show *LCST* behaviour upon heating to 300°C. The clarity of the melt and the glass transition behaviour clearly show that PDPS is miscible with PCMMA and PCEMA.

Poly(2,2-dimethyl-1,3-propylene adipate) blends

Blends of PDPA with PCMMA and PCEMA were clear. Once melted, PDPA crystallizes very slowly at room temperature[19]. Thus the clarity of the blends indicates that the blends are likely to be miscible. Each of these blends showed one T_g, confirming the miscibility.

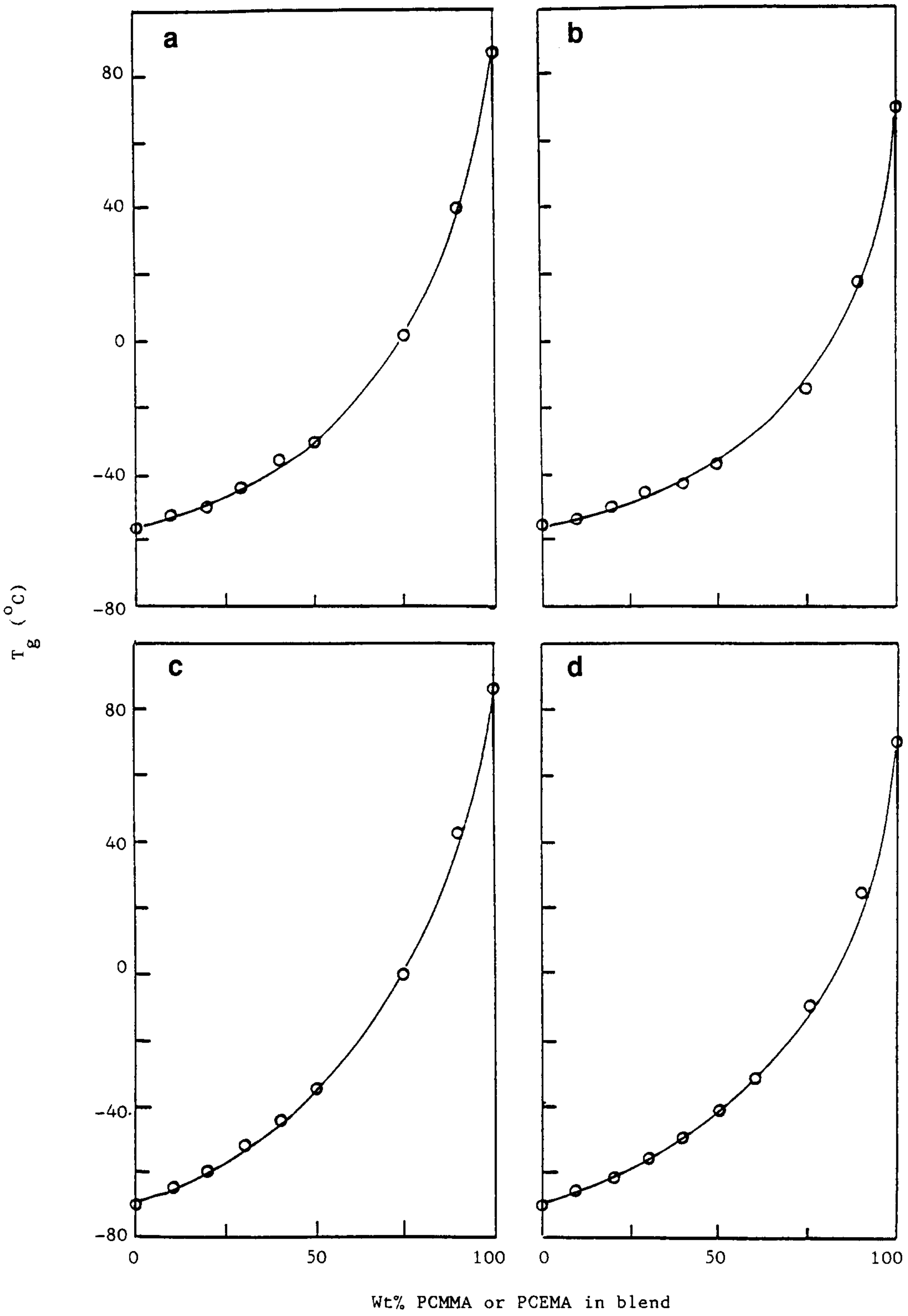

Figure 2 T_g *versus* composition curves for blends: (a) PCMMA/PEA; (b) PCEMA/PEA; (c) PCMMA/PBA; (d) PCEMA/PBA

The T_g *versus* composition curves are shown in *Figures 3c* and *3d*. *LCST* behaviour was not observed for the blends.

Poly(2,2-dimethyl-1,3-propylene sebacate) blends

PCMMA/PDPSb blends were clear and each blend showed a single T_g, indicating that PCMMA is miscible with PDPSb. *Figure 4a* shows the T_g *versus* composition curve of the blends. In contrast, PCEMA/PDPSb blends were cloudy and each blend showed the existence of two glass transitions. However, these cloudy blends turned clear when heated to the region of 65–90°C, showing the existence of upper critical solution temperature (*UCST*) behaviour; the cloud point curve is shown in *Figure 5*. Upon cooling to room temperature, cloudiness redeveloped within a day. The cloudiness is not the result of crystallization of PDPSb as the melting point of the polyester is below room temperature. Furthermore, if the clear blends were kept at 60°C, they reverted to cloudiness within 20 min. It is interesting to note that some blends of PDPA and PDPS show *UCST* behaviour[20].

To our knowledge, there are no reports on the

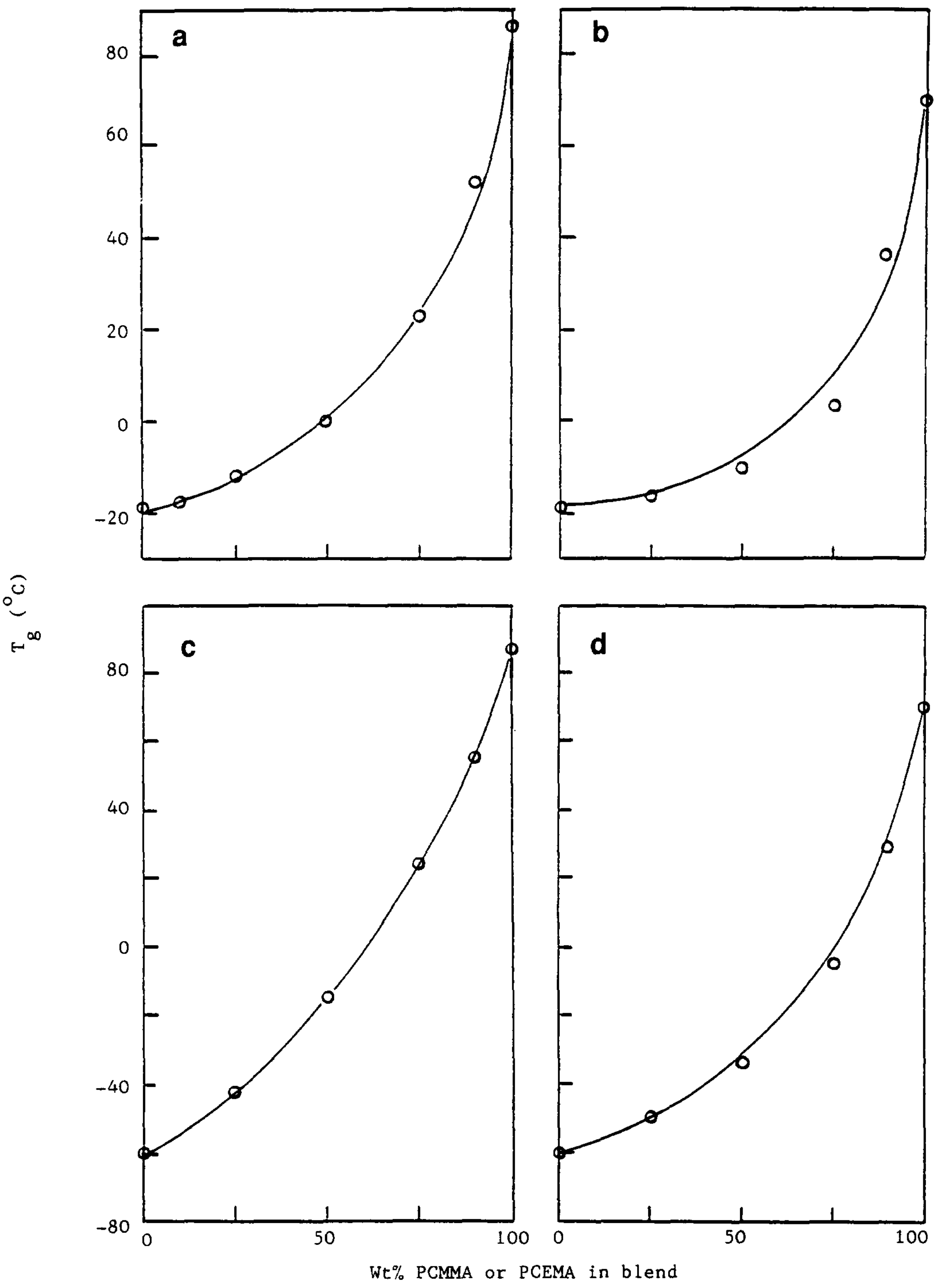

Figure 3 T_g *versus* composition curves for blends: (a) PCMMA/PDPS; (b) PCEMA/PDPS; (c) PCMMA/PDPA; (d) PCEMA/PDPA

miscibility of PVC with PDPSb and therefore we also examined the miscibility behaviour of these blends. All the PVC/PDPSb blends were clear. The existence of a single T_g in each blend confirms that PVC is miscible with PDPSb. The T_g *versus* composition curve is shown in *Figure 4b*.

Poly(hexamethylene sebacate) blends

All the blends were cloudy but they turned clear upon heating above the melting point of PHS. The T_gs of blends with high PHS contents were difficult to observe due to the high crystallinity and rapid crystallization of PHS. However, the transparency of the melt is a good indication that the blends are miscible. Furthermore, the melting point depression behaviour of the blends, as discussed in the next section, also shows that PHS is miscible with PCMMA and PCEMA.

Melting point depression analysis

For a miscible blend containing a crystallizable component, the melting point depression of the crystalline polymer by the miscible diluent is used to evaluate the polymer–polymer interaction parameter χ, and interaction density B using the equations[21]:

$$T_m = T_m^\circ + B(V_{2u}/\Delta H_{2u})T_m^\circ \phi_1^2$$

$$\chi = BV_{1u}/RT_m^\circ$$

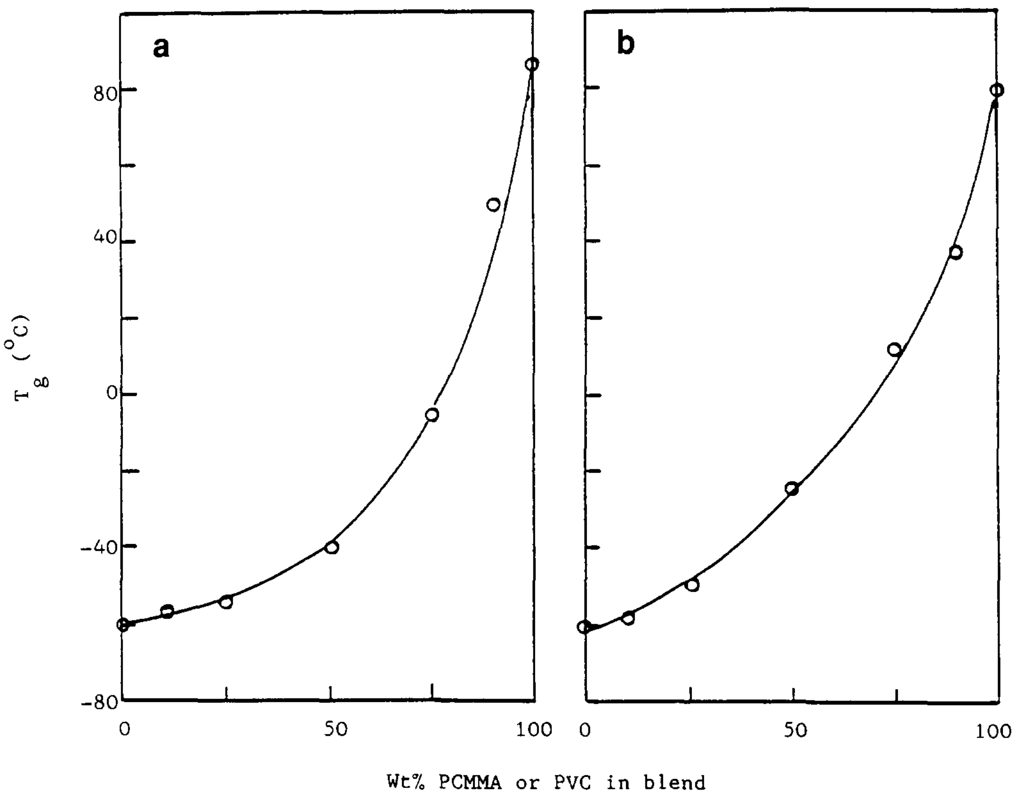

Figure 4 T_g *versus* composition curves for blends: (a) PCMMA/PDPSb; (b) PVC/PDPSb

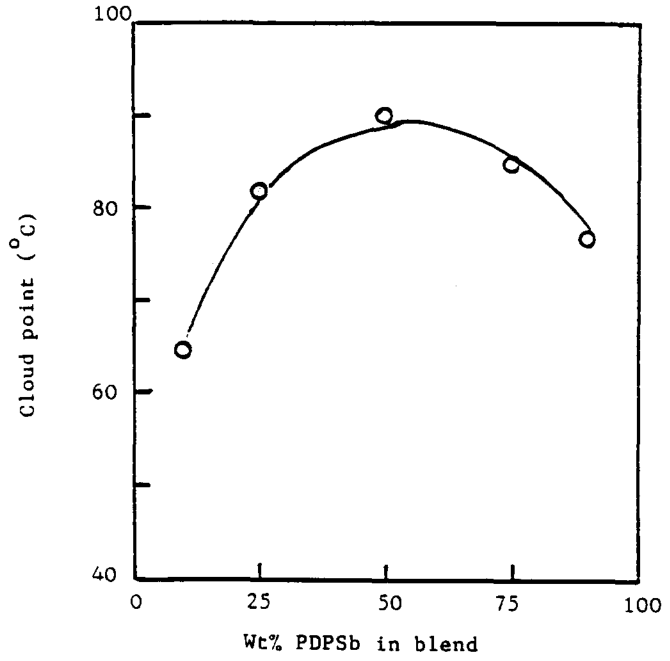

Figure 5 Cloud point curve for PCEMA/PDPSb blends

where the subscripts 1 and 2 refer to the amorphous polymer and the crystalline polymer, respectively; ΔH_{2u} is the heat of fusion per mole of crystalline repeating units; V_{1u} and V_{2u} are the molar volumes of repeating units; ϕ_1 is the volume fraction of component 1 in the blend; T_m and T_m° are the equilibrium melting points of the blend and the pure crystalline polymer, respectively.

The equilibrium melting point of a sample is determined by the Hoffman–Weeks method in which the observed melting points (T_m) are plotted as a function of crystallization temperatures (T_c) and extrapolated to intersect with the $T_m = T_c$ line to obtain the equilibrium melting point. *Figures 6a* and *6b* show the Hoffman–Weeks plots for PCMMA/PHS and PCEMA/PHS blends, respectively, and *Figure 7* shows the melting point depression plots for the two blend systems. Using $\Delta H_{2u}/V_{2u} = 156.4$ J cm^{-3} for PHS[22], $V_{1u(\mathrm{PCMMA})} = 99.6$ cm^3 mol^{-1}, $V_{1u(\mathrm{PCEMA})} = 113.3$ cm^3 mol^{-1}, density $\rho_{\mathrm{PCMMA}} = 1.35$ g cm^{-3}, $\rho_{\mathrm{PCEMA}} = 1.32$ g cm^{-3} and $\rho_{\mathrm{PHS}} = 1.03$ g cm^{-3}, the χ values were found to be -1.20 and -0.76 for PCMMA/PHS and PCEMA/PHS blends, respectively. The corresponding B values are -34.9 and -19.4 J cm^{-3}. The values suggest that the interaction in PCMMA/PHS blends is more intense than that in PCEMA/PHS blends. A similar trend has also been observed for PCMMA/PCL and PCEMA/PCL blends[9]. It has been reported that the B value is -3.8 cal cm^{-3} (-15.9 J cm^{-3}) for PVC/PHS blends[17]. This value is less negative than that for PCMMA/PHS blends and comparable to that for PCEMA/PHS blends.

The melting point depression analysis was not carried out for blends with PDPA and PDPSb as these polyesters crystallize very slowly. Blends containing PDPS, PBA and PEA showed complex melting endotherms and hence no further work was done.

SUMMARY

Table 2 summarizes the miscibility behaviour of PVC, PCMMA and PCEMA with polyesters. The results once again illustrate the similarity in the miscibility behaviour of the three polymers. Those polyesters which are miscible with PVC are also miscible with PCMMA and PCEMA. In addition, PCMMA is miscible with polyesters having small CH_2/COO ratios such as PES and PEA.

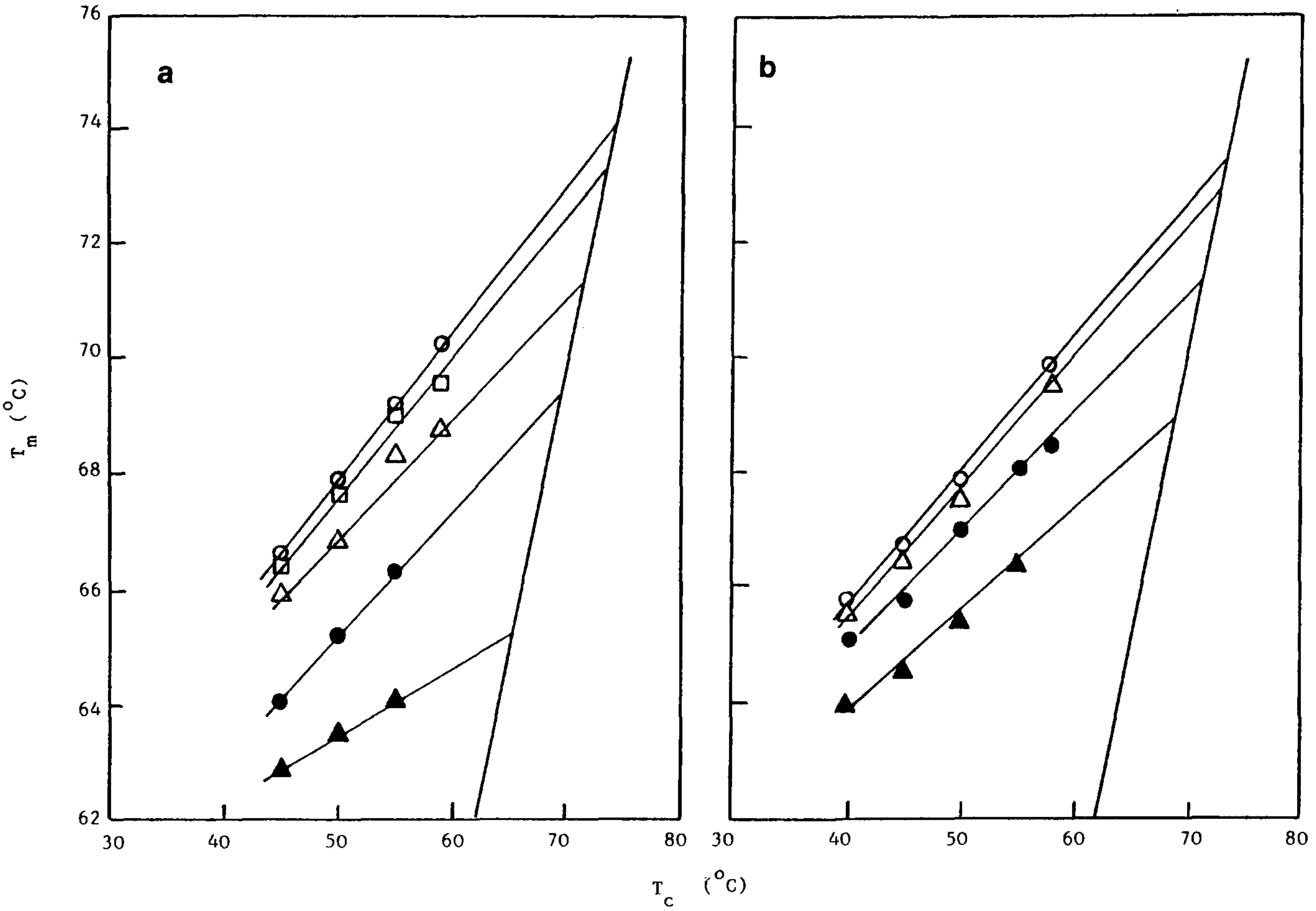

Figure 6 Hoffman–Weeks plots. (a) PCMMA/PHS blends: ○, 100% PHS; □, 90% PHS; △, 80% PHS; ●, 70% PHS; ▲, 60% PHS. (b) PCEMA/PHS blends: ○, 90% PHS; △, 80% PHS; ●, 70% PHS; ▲, 60% PHS

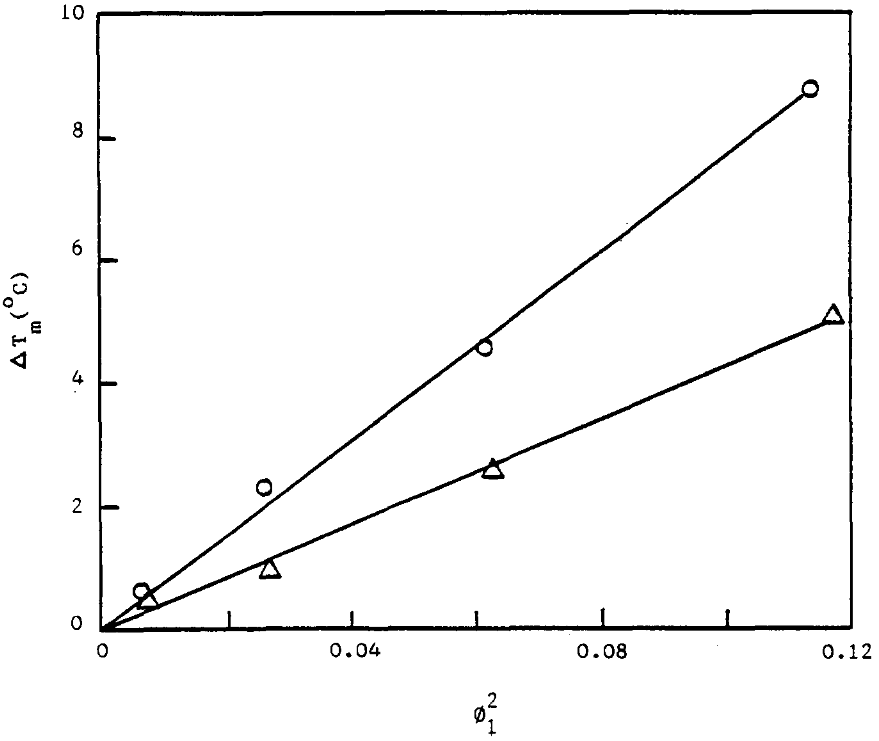

Figure 7 Melting point depression plots for PCMMA/PHS (○) and PCEMA/PHS (△) blends

Table 2 Miscibility behaviour of blends

Polyester (CH_2/COO ratio)	PVC	PCMMA	PCEMA
PES (2)	Immiscible[16]	Miscible	Immiscible
PEA (3)	Immiscible[16]	Miscible	Miscible
PBA (4)	Miscible[16]	Miscible	Miscible
PCL (5)	Miscible[7,16]	Miscible[9]	Miscible[9]
PDPS (3.5)	Miscible[16]	Miscible	Miscible
PDPA (4.5)	Miscible[24]	Miscible	Miscible
PDPSb (6.5)	Miscible	Miscible	*UCST* behaviour
PHS (7)	Miscible[16]	Miscible	Miscible

Recently, Coleman *et al.*[23] proposed a general guide to predict polymer–polymer miscibility based on the 'non-hydrogen bonded' solubility parameter concept. For polymers interacting with weak dispersive force only, the non-hydrogen bonded solubility parameters (δ) of the two polymers must be closely matched [$\Delta\delta < 0.2$ $(\mathrm{J\,cm^{-3}})^{1/2}$] in order to form a miscible blend. For polymers able to interact with stronger interactions, a larger mismatch between δ can be tolerated. They used this concept to explain the miscibility of PVC/polyester blends. Using the group molar attraction constants given by Coleman *et al.*[23], the values for PCMMA and PCEMA are calculated to be 20.7 and 20.0 $(\mathrm{J\,cm^{-3}})^{1/2}$, respectively. These values are very close to that of 20.2 $(\mathrm{J\,cm^{-3}})^{1/2}$ for PVC[23]. The similar δ values of the three polymers may account for their similar miscibility behaviour.

ACKNOWLEDGEMENT

Financial support of this research by the National University of Singapore is gratefully acknowledged.

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