Miscibility of caprolactone/ethylene terephthalate copolymers with chlorinated polymers: a differential scanning calorimetry and Fourier transform infra-red study

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Differential scanning calorimetry was used to determine the miscibility and phase behaviour of poly(ethylene terephthalate-co-caprolactone)/chlorinated polymer blends. Five copolymers differing in poly(ethylene terephthalate) (PET) content were blended with poly(vinyl chloride) (PVC), a chlorinated PVC (CPVC) with a chlorine content of 67.2% and a chlorinated polyethylene (PECL) with a chlorine content of 48%. The results show that CPVC is miscible with each of the copolymers investigated, provided that the blends are annealed between T_g and their lower critical solution temperature (LCST). However, PVC is only miscible with copolymers containing 33 and 44% PET, whereas PECL is miscible only with the copolymer containing 33% PET. Miscibility is more easily achieved with chlorinated polymers of a high chlorine concentration. A LCST was observed with blends of CPVC with copolymers containing 64 and 89% PET. Furthermore the LCST of the former blend occurs at a higher temperature than that of the latter. This difference is caused by a decrease of intermolecular interactions and/or intramolecular repulsions, which coexist in these mixtures. A LCST was also observed in blends of PECL with the copolymer containing 33% PET. Some measurements were made with PET/poly(caprolactone) blends, which were found to be immiscible, and the importance of specific interactions (attractive and repulsive) are discussed.

(Keywords: miscibility; copolymers; phase behaviour; polymer blends)

INTRODUCTION

It has been shown that linear polyester/chlorinated polymer blends exhibit a miscibility window defined by an optimum ratio of the number of methylene groups to the number of carbonyl groups (or CH_2/COO ratio on each repeat unit)[1–5]. Outside this window, at low and high CH_2/COO ratios, immiscibility is found. Inside this window, poly(caprolactone) (PCL), for example, is miscible with a large number of chlorinated polymers provided that their chlorine content is sufficiently high.

It has been shown that the miscibility between these two series of polymers is related to the presence of specific intermolecular interactions between PCL and the chlorinated polymers. FTi.r. spectroscopy[6–9] indicates that the carbonyl group of the polyester participates in the interaction. A hydrogen-bonding interaction between the carbonyl groups of the polyester and the α-hydrogens of the chlorinated polymer has often been postulated, and recent measurements made on model compounds support this proposal[10]. Inverse gas–liquid chromatography[11] indicates that the interaction between polyesters and chlorinated polymers involves the presence of chlorine atoms. However, FTi.r. spectroscopy[12] measurements of PCL/poly(vinylidene chloride-co-acrylonitrile) blends have led to the suggestion of the presence, also, of a hydrogen-bonding interaction between the carbonyl groups of the polyester and the β-hydrogens of the chlorinated polymer. In fact, we believe that several types of interactions, hydrogen bonding and dipole–dipole

interactions, can act simultaneously and contribute to the miscibility, although their relative importance can be very different from system to system[10].

With aromatic polyester/chlorinated polymer blends, Aubin and Prud'homme[13] have shown, using poly(ethylene terephthalate) (PET), poly(butylene terephthalate) and poly(hexamethylene terephthalate), that their behaviour is the same as that of linear polyesters: a high concentration of chlorine atoms is similarly required to achieve miscibility, and there is a miscibility window in terms of the carbonyl polyester concentration.

Moreover, recent theoretical and experimental investigations[14–16] have dealt with the observation that random copolymers often form miscible blends with other polymers whereas the corresponding homopolymers do not. For example, several authors[17–19] have established that PCL is miscible with styrene/acrylonitrile copolymers over a certain range of acrylonitrile contents, but neither poly(styrene) nor poly(acrylonitrile) is miscible with PCL. Therefore, it is concluded that the presence of intramolecular repulsions between the styrene and acrylonitrile repeat units of the copolymer makes it miscible with PCL. In this case, the presence of specific interactions is not the driving force towards miscibility. Rather, we have 'specific repulsions'.

Recently, a series of poly(ethylene terephthalate-co-caprolactone) (TCL) of different compositions has been synthesized[20]. This series of polymers can be useful to investigate the miscibility behaviour of caprolactone copolymers and the effect of reducing the caprolactone unit concentration, without reducing significantly the

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Table 1 Polymers used in this study

| Polymers	Acronym	PET content (wt%)	$[\eta]^a$ (dl g^{-1})	M_w (kg mol^{-1})	T_g (°C)
Poly(ethylene terephthalate-*co*-caprolactone)	TCL33	33	1.36	–	–34
Poly(ethylene terephthalate-*co*-caprolactone)	TCL40	40	0.88	–	–11
Poly(ethylene terephthalate-*co*-caprolactone)	TCL55	55	0.80	–	9
Poly(ethylene terephthalate-*co*-caprolactone)	TCL64	64	0.72	–	20
Poly(ethylene terephthalate-*co*-caprolactone)	TCL89	89	0.68	–	37
Poly(vinyl chloride) (56 wt% Cl)	PVC	–	–	80	83
Chlorinated PVC (67 wt% Cl)	CPVC	–	–	100	129
Chlorinated polyethylene (48 wt% Cl)	PECL	–	–	–	10
Poly(caprolactone)	PCL	–	–	36	–64
Poly(ethylene terephthalate)	PET	–	–	58	81

^{a} Measured in *m*-cresol at 30°C
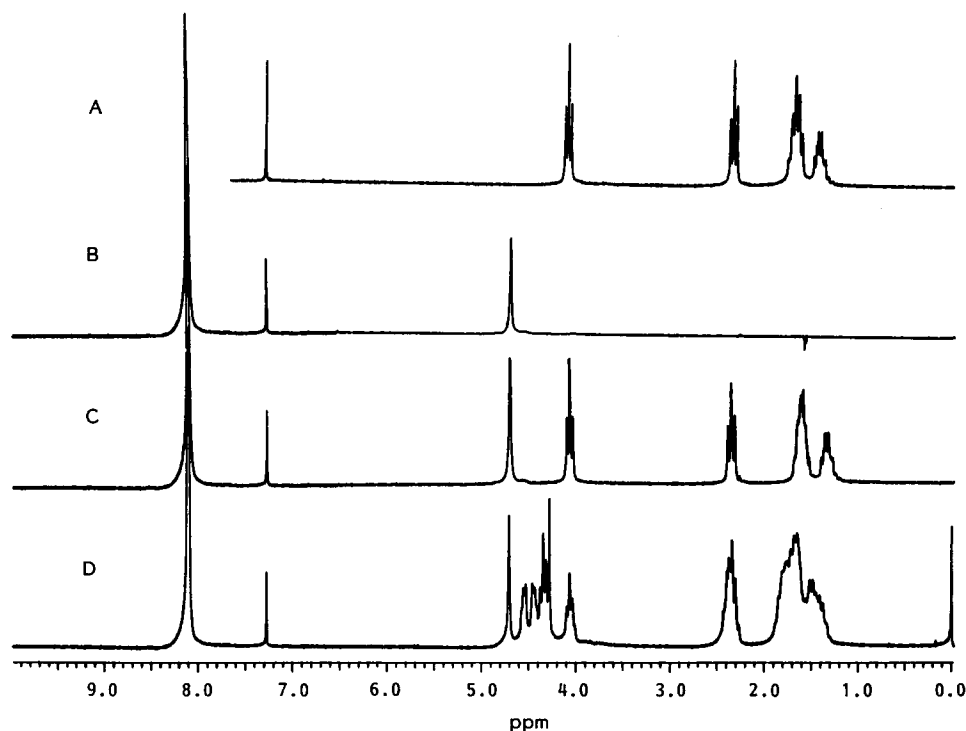
Figure 1 200 MHz proton spectra of (A) PCL, (B) PET, (C) a PET/PCL blend and (D) TCL40 at 25°C. The solvent is a mixture of deuterated chloroform and trifluoroacetic acid (9:1)

carbonyl concentration since the second repeat unit is also a polyester. In this study, TCL samples were blended with poly(vinyl chloride), chlorinated poly(vinyl chloride) and a chlorinated polyethylene. These different mixtures have been analysed by differential scanning calorimetry (d.s.c.) and Fourier transform infra-red (*FT*i.r.) spectroscopy. It will be shown that both the 'intermolecular specific interactions' and the 'intramolecular specific repulsions' contribute to the relative miscibility and phase behaviour of these systems as a function of composition and temperature.

EXPERIMENTAL

A list of the polymers used in the present study with their weight-average molecular weight M_w, intrinsic viscosity [η], glass transition temperature T_g and PET content is given in *Table 1*. The copolymers were synthesized at the University of Science and Technology of China[20]. The synthesis is divided into two steps: the first involves the esterification of terephthalic acid and ethylene glycol; the second is a polycondensation of ethylene terephthalate with caprolactone in the presence of a catalyst. Poly(vinyl chloride) (PVC) was obtained from Shawinigan Chemicals, the chlorinated PVC (CPVC) was supplied by the BF Goodrich Chemical Division, and the chlorinated polyethylene (PECL), PCL and PET were purchased from Aldrich Chemicals.

The copolymers were purified by precipitation in methanol from a 5% (w/v) chloroform solution. Their PET content was determined by nuclear magnetic resonance spectroscopy from a 5% deuterated chloroform solution at room temperature with a Varian XL-200 spectrometer. For illustration, one of the proton spectra of the TCL copolymers is given in *Figure 1*. The peaks centred at 2.34 and 8.10 ppm correspond, respectively, to protons of the methylene group next to the carbonyl group in PCL and to the benzene ring of PET. They were used for the determination of the PET content of the copolymers. We can also note that, in the 4.0–4.7 ppm

Table 2 D.s.c. analysis of TCL copolymer/chlorinated polymer blends after annealing 3 min at 150°C

TCL copolymer	Chlorinated polymer in blend (wt%)	T_g (°C) With CPVC	With PVC	With PECL
TCL33	100	129	83	10
	80	78	47	2
	60	42	24	−9
	30	19	12	−14
	40	6	1	−20
	20	−21	−20	−30
	0	−34	−34	−34
TCL40	100	129	83	n.d.
	70	64	42	n.d.
	50	40	25	n.d.
	30	14	9	n.d.
	0	−11	−11	n.d.
TCL55	100	129	83	n.d.
	70	75	18, 35	n.d.
	50	37	26, 48	n.d.
	30	22	38, 69	n.d.
	0	9	9	n.d.
TCL64	100	129	83	n.d.
	70	80	24, 48	n.d.
	50	45	32, 57	n.d.
	30	25, 84	42, 70	n.d.
	0	20	20	n.d.
TCL89	100	129	83	10
	70	91	32, 77	12, 35
	50	41, 110	42, 82	13, 35
	30	37, 112	44, 81	13, 37
	0	37	37	37

n.d.: not determined

region, there are several peaks that are not present in the homopolymers[20], confirming that these products are really copolymers and not a mixture of two homopolymers. In all copolymers, PCL is unable to crystallize. In TCL55, TCL64 and TCL89 samples, the PET unit is able to crystallize although the crystallization is so slow that we usually got amorphous samples.

Blends were prepared by slowly casting films from a dichloromethane solution at room temperature. The resulting films were dried in a vacuum oven at room temperature until they reached constant weight. This procedure appears to be satisfactory since it led to the same T_g values for the homopolymers (PVC, CPVC and PECL) as those obtained with the initial dried powder (see *Table 2*).

D.s.c. measurements were conducted with a Perkin–Elmer DSC-4 apparatus equipped with a TADS microcomputer. The d.s.c. was calibrated with ultrapure indium. The glass transition temperatures (T_g) were recorded at the half-height of the corresponding heat capacity jump. In the d.s.c. apparatus, the samples were first cooled at −100°C and maintained at that temperature for 5 min. They were then heated up at a rate of 20°C min⁻¹ to 150°C and kept at that temperature for 3 min. The samples were finally quenched at a rate of 320°C min⁻¹ to −100°C and reheated to 150°C. In this paper, the following terminology is retained: a sample is considered miscible if it gives at each composition a single T_g intermediate between those of the individual components. Thus, a sample exhibiting two T_g values at a given composition is considered immiscible, even if the possibility of observing a single T_g at other compositions is not excluded.

Phase separation was investigated by d.s.c. with the following annealing cycle. The samples were first cooled to −100°C and maintained at that temperature for 5 min. A first scan was made at a heating rate of 200°C min⁻¹ up to an annealing temperature close to the highest T_g of the homopolymers considered. The sample was maintained for 3 min at that temperature and quenched to −100°C. It was again left 5 min at this temperature before a second scan, at a heating rate of 20°C min⁻¹, to an annealing temperature 10 or 20°C above the annealing temperature of the previous scan. Such a heating–cooling cycle was repeated until two well defined T_g values could be observed. The annealing temperature at which two T_g values begin to be observed corresponds approximately to the cloud point of the sample.

*F*T.i.r. measurements were made with a Mattson Sirius-100 spectrometer. Thin films were cast onto a NaCl window from 0.5% (w/v) dichloromethane solutions. After evaporation of most of the solvent, the films were transferred to a vacuum desiccator and kept at room temperature for 24 h to remove the residual solvent. The spectra were measured at room temperature, except for the spectrum of molten PCL, which was recorded at 80°C using a high-temperature cell connected to an Omega D-921 thermoregulator. All spectra (200 scans) were recorded with a resolution of 2 cm⁻¹, signal-averaged and stored on a magnetic disc system. The films used in this study were sufficiently thin to obey the Beer–Lambert law.

RESULTS

Table 2 lists the T_g values of CPVC/TCL, PVC/TCL and PECL/TCL blends prepared at an annealing temperature of 150°C. According to the single T_g criterion, blends with TCL33, CPVC and PVC blends with TCL40, and CPVC blends with TCL55 are miscible. In each of these examples, the T_g of the blends changes smoothly with composition. For example, the T_g–composition curve of CPVC/TCL33 blends is given in *Figure 2*. It can be described by the Gordon–Taylor equation. However, the blends with TCL64 and TCL89 exhibit two T_g values at some compositions and immiscibility.

Furthermore, when the samples are annealed at different temperatures, a cloud-point curve can, in many instances, be detected. For example, in *Figure 3* are given the thermograms of a CPVC/TCL64 blend having a TCL64 content of 30%. The thermograms obtained after
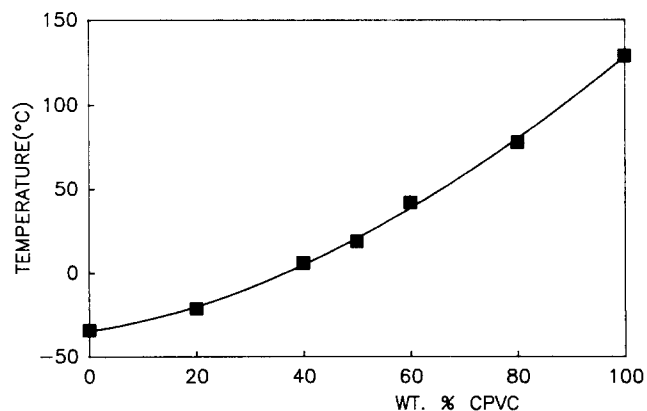
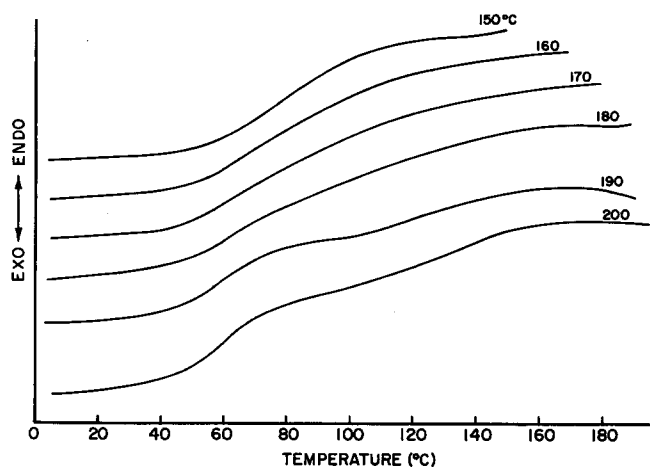**Figure 2** Glass transition temperature–composition curve of the TCL33/CPVC blend

Figure 3 D.s.c. thermograms of TCL64/PVC (30/70) blends that were annealed 3 min at the temperature indicated, before quenching and scanning
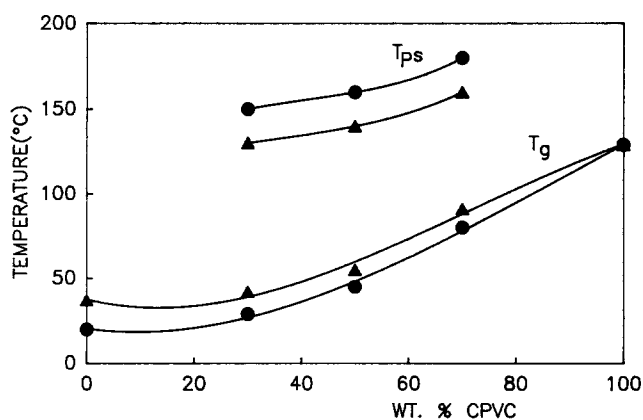

Figure 4 Phase behaviour of TCL64/CPVC (●) and TCL89/CPVC (▲) blends as a function of composition; T_g is the glass transition temperature and T_{ps} the temperature of phase separation

annealing at 150, 160 and 170°C show a single T_g, which is relatively broad. But two distinguishable T_g values appear at annealing temperatures between 180 and 200°C. Therefore, a thermally induced phase separation occurs for this blend at a temperature between 170 and 180°C.

Similar experiments were conducted with other compositions and other blends. *Figure 4* illustrates the phase behaviour of CPVC/TCL64 blends as a function of composition. For CPVC/TCL64 blends, a temperature of phase separation (T_{ps}) is observed at each composition in the 150–180°C range. The phase separation then occurs at relatively high temperatures and, after annealing at 150°C (as done in *Table 2*), one obtains a single composition-dependent T_g intermediate between those of the corresponding homopolymers, except at a TCL64 content of 70% where the temperature of annealing is above T_{ps} (*Figure 4*). This latter sample is, however, miscible if it is annealed at slightly lower temperatures.

Figure 4 also illustrates a similar phase behaviour with CPVC/TCL89 blends. In this case, the temperature of phase separation is in the 130—160°C range. This temperature range of phase separation appears below that of CPVC/TCL64 blends. Thus, at two compositions, for an annealing temperature of 150°C, two distinguishable T_g values were observed (*Table 2*). Again, only one

T_g (and miscibility) is found with this system, at any composition, if the samples are annealed at sufficiently low temperatures; this means that CPVC is miscible with each of the copolymers investigated in this study, at any condition, provided that the samples are annealed at low enough temperatures. With the other copolymers, no T_{ps} is observed upon heating the samples before the decomposition temperature of CPVC.

A similar behaviour was found with PVC, but with a lesser degree of miscibility. The T_g-composition curve of TCL40/PVC blends is shown in *Figure 5*. The single T_g of these blends varies regularly with composition. However, PVC blended with TCL55, TCL64 and TCL89 is found to be immiscible at any composition (between 30 and 70%), even after annealing at temperatures as low as 80°C.

The behaviour of PECL blends with TCL copolymers is more ambiguous, because the T_g values of the components in blends with TCL40, TCL55 and TCL64 are very close to each other and cannot be detected separately. From *Table 2*, it is seen that PECL is immiscible with TCL89 but miscible with TCL33. The latter blends also exhibit a lower critical solution temperature (*LCST*), as shown in *Figure 6*, in the 240–260°C range. This phase separation occurs at sufficiently high temperature to permit the observation of a single T_g at all compositions for an annealing temperature of 150°C. Similar results were obtained with
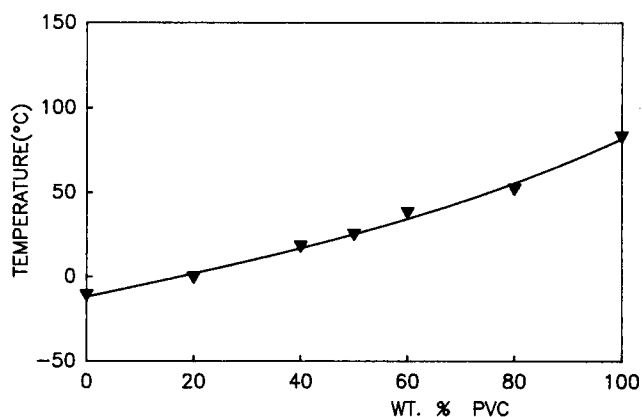

Figure 5 Glass transition temperature–composition curve of the TCL40/PVC blend
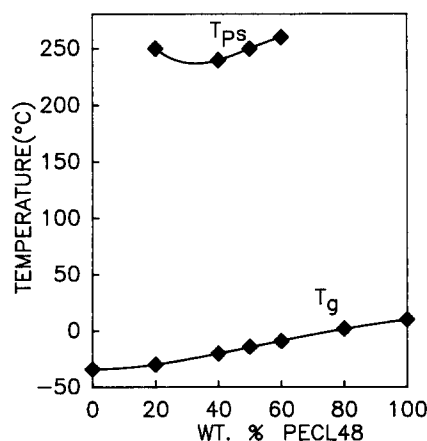

Figure 6 Phase behaviour of TCL33/PECL blends as a function of composition; T_g is the glass transition temperature and T_{ps} the temperature of phase separation
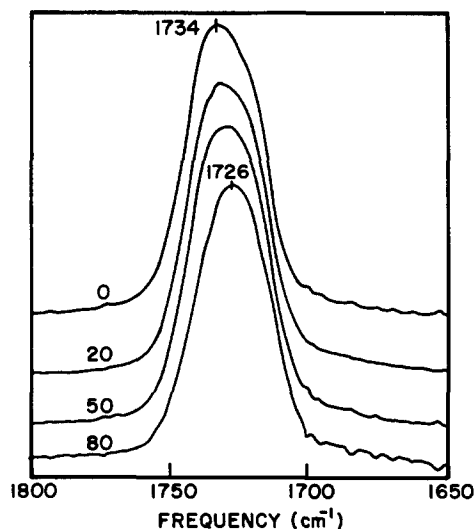
Figure 7 *F*Ti.r. spectra of TCL33/CPVC blends in the 1800–1650 cm^{-1} region at room temperature; the numbers correspond to the per cent CPVC in those blends

Table 3 Frequency of the carbonyl stretching band (cm^{-1}) in spectra of TCL33/chlorinated polymer and PCL/chlorinated polymer blends at room temperature

| Copolymer | wt% | Chlorinated polymer | | |
		CPVC	PVC	PECL
TCL33	20	1726	1726	1728
TCL33	40	1727	1727	1729
TCL33	50	1728	1728	1730
TCL33	60	1728	1728	1738
TCL33	80	1730	1732	1733
TCL33	100	1734	1734	1734
PCL	20	1730	1730	1733
PCL	100^a	1734	1734	1734

^{a} Taken at 80°C

another PECL, containing 42 wt% Cl, blended with pure PCL[21]. In contrast, PECL/TCL89 blends exhibit two T_g values, whatever the annealing temperature used.

The miscibility of the samples mentioned above has been confirmed by *F*Ti.r. measurements. All samples exhibiting a single T_g also lead to a shift of the carbonyl stretching band of the polyester. A specific example is shown in *Figure 7* with TCL33/CPVC blends, where it is seen that the maximum of the peak is shifted by 8 cm^{-1} as compared to the peak position observed with the pure copolymer, for a blend containing 80% of CPVC. Other similar results are summarized in *Table 3* with PVC and PECL polymers. Immiscible blends did not give any shift with composition.

DISCUSSION AND CONCLUSIONS

Table 4 summarizes the results obtained by d.s.c. in the present study concerning the miscibility behaviour of TCL copolymer/chlorinated polymer blends. CPVC is miscible with each of the copolymers investigated, provided that the blends are treated at the appropriate temperature, between T_g and T_{ps}. However, PVC is only miscible with the TCL33 and TCL40 copolymers. Finally, PECL is miscible with the TCL33 copolymer, but this blend undergoes phase separation above 240°C. These results show that miscibility is more easily achieved with

chlorinated polymers having high chlorine concentrations (2–4).

This conclusion is confirmed by the *F*Ti.r. data. From *Table 3*, one can see that CPVC and PVC blends exhibit the same shift of the carbonyl vibration band. However, for PECL blends, the shifts are smaller. A recent n.m.r. study[22] has shown that CPVC contains 67.2 wt% chlorine atoms, with about twice as many CHCl as CH$_2$ groups, and about 7% of CCl$_2$ groups. Therefore, it is likely that hydrogen bonding between the α-hydrogens of the chlorinated polymer and the carbonyl groups of the TCL copolymer is the principal intermolecular interaction, although other weaker interactions such as hydrogen bonding with the β-hydrogens of the chlorinated polymer and dipole–dipole interactions cannot be discarded at this moment.

A *LCST* can be observed in mixtures with intermolecular specific interactions or in mixtures with intramolecular specific repulsions[23–25]. In both cases, the phase separation has been explained by a variation of the thermodynamic interaction parameter χ, which becomes positive above the *LCST*. According to Patterson[26,27], χ can be expressed by two factors: an interactional contribution, which is associated with the 'complementary dissimilarity' between the components; and a free-volume contribution, which follows from a difference in thermal expansion of the compounds. In mixtures without 'complementary dissimilarity', the interactional contribution can be related to intramolecular repulsions[14–16]. Phase separation takes place on raising the temperature because the free-volume contribution becomes more positive and the interactional contribution becomes less negative owing to the dissociation of the specific interactions or to the weakening of the intramolecular repulsions.

As described above, a *LCST* was observed for CPVC blends with TCL64 and TCL89 copolymers. Furthermore, the *LCST* of the TCL89 blends occurs at a temperature that is lower than that found with TCL64 blends. This difference is caused by a decrease of intermolecular interactions and/or intramolecular repulsions since, in these mixtures, they coexist. The fact that a *LCST* cannot be observed in CPVC and PVC blends with the TCL33 copolymer, but that it is seen in PECL blends with TCL33 copolymer at a temperature of about 240°C, demonstrates that the intermolecular interactions are relatively weak with the PECL blends as compared to those with PVC and CPVC. Stronger interactions tend to shift the *LCST* upwards to increase the miscibility temperature zone, as demonstrated theoretically[26].

We have also attempted to evaluate the contribution of PET units to the miscibility of TCL blends with

Table 4 Miscibility behaviour of poly(ethylene terephthalate-*co*-caprolactone)/chlorinated polymer blends; miscibility means that there is a certain temperature range where blends are miscible over the full composition range (see text for details)

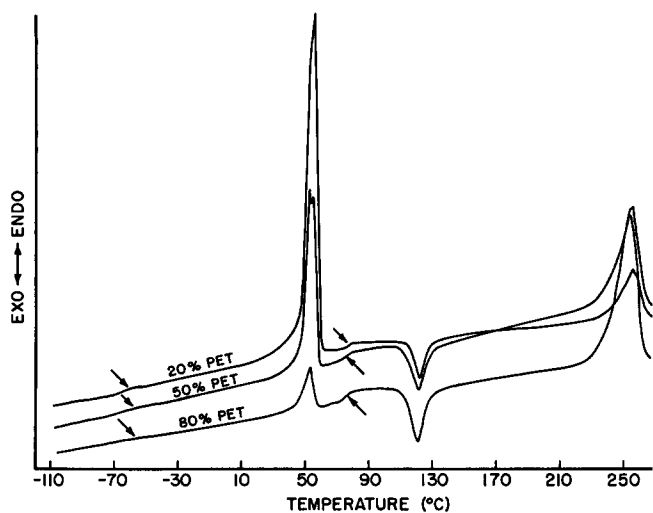| Copolymer	CPVC	PVC	PECL
TCL33	M	M	M
TCL40	M	M	–
TCL55	M	I	–
TCL64	M	I	–
TCL89	M	I	I

M means miscibility and I immiscibility

Figure 8 D.s.c. thermograms of PET/PCL blends prepared in o-dichlorobenzene. Each blend was annealed at 280°C for 3 min, then quenched to −120°C before scanning

Table 5 Reduced parameters and other useful data

	α (K^{-1} × 10^4)	$\tilde{V}$	T^* (K)	τ^2
PCL (at 120°C)	7.2^a	1.2371	7 106	
				0.0407
PVC (at 120°C)	5.0^b	1.1734	8 903	
				0.1467
PET (at T_g=70°C)	3.1^c	1.0975	12 313	

^{a} From ref. 28; ^{b} from ref. 29; ^{c} from ref. 30

chlorinated polymers. *Figure 8* shows d.s.c. thermograms of PET/PCL blends at three different compositions. In all cases, there are two T_g values (shown by the arrows); moreover, the values of T_g are very close to the values of T_g of the corresponding components. Therefore, it can be concluded that PET and PCL homopolymers are immiscible. Then, following the theory of intramolecular specific repulsions[14–16], we have to consider not only the formation of carbonyl/CHCl interactions but also the intramolecular repulsions between PET and PCL structural units to explain the miscibility in blends of TCL copolymers with chlorinated polymers. In agreement with this proposal, we notice that the shifts of the C=O band reported in *Table 3* are larger with the copolymers than they are with pure PCL. For example, with PVC, the shift of the blend containing 20% PCL is of 4 cm^{-1} with respect to the position of the carbonyl band of pure PCL, as compared to a shift of 8 cm^{-1} for the blend containing 20% TCL33 with respect to the position of the carbonyl band of pure TCL33. The same behaviour is observed with each of the three chlorinated polymers investigated, taken separately. This strongly suggests that the intramolecular repulsions between PET and PCL units are significant.

In general, we can say that the addition of a chlorinated polymer to TCL copolymers is favoured at high caprolactone concentration, since PCL/chlorinated polymer blends are miscible, and since PET/PCL intramolecular repulsions also contribute to favour the miscibility. At low caprolactone concentrations in the copolymers, the repulsive PET/chlorinated polymer interactions become dominant and can lead to immiscibility; PET/chlorinated polymer blends can be miscible only in the case where the chlorine concentration of chlorinated polymer is larger than about 62%.

Why, then, is PET less miscible with chlorinated polymers than PCL? First, it is well known that PCL exhibits an optimum CH$_2$/COO ratio, which leads to strong COO/CHCl interactions between PCL and PVC, although the precise reason for the presence of the optimum ratio is not clear[6]. It is evident that PET does not exhibit such an optimum ratio and, therefore, the hydrogen-bond interactions between PET and PVC units are weaker. However, at the same time, the amount of

CHCl groups (and the number of α-hydrogens available in CPVC) is larger than that in PVC[22], and, therefore, PET can be miscible with CPVC. Generally, as shown by Patterson[26,27], interactional contributions to mixing in blends can be divided into two parts: a contribution of dispersion forces and a contribution of specific interactions. Both contributions lead to variations of the enthalpy of mixing: positive and unfavourable to mixing for dispersion forces, and negative and favourable in the case of specific interactions. On the basis of previous studies of polyester/chlorinated polymer blends[5,28], it seems that in PCL/PVC blends the specific interactions are strong and the dispersion forces relatively weak; but in the PET/PVC system, the situation appears to be the reverse.

Secondly, according to the equation-of-state theory, the large difference of free volume between components in blends is an unfavourable condition for mixing. Patterson has suggested the following approximate relation for the free-volume component of the interaction parameter χ[26]:

$$\chi = C_p/2R\tau^2 \tag{1}$$

$$\tau = (1 - T_1^*/T_2^*) \tag{2}$$

$$T^* = T[V^{4/3}/(V^{1/3} - 1)] \tag{3}$$

$$V = [(3 + 4\alpha T)/(3 + 3\alpha T)]^3 \tag{4}$$

and C_p is the configurational heat capacity, T_i^* the characteristic temperature of polymer i, V the reduced volume and α the thermal expansion coefficient at temperature T. Using the experimental data found in the literature, a simple calculation gives the results shown in *Table 5*. One can see that the value of τ for the PET/PVC pair is much larger than that for the PCL/PVC pair, meaning that the free-volume effect in the second case does not oppose mixing as much.

Therefore, it seems probable that the immiscibility of PET/PVC blend, as compared to the miscibility of the PCL/PVC blends, is due to a combination of weaker specific interactions and stronger free-volume contribution.

ACKNOWLEDGEMENTS

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