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Phase behaviour of blends of polyesters and polycarbonates

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The phase behaviour of binary blends of polyesters and polycarbonates has been reviewed with reference to predictions of the enthalpic interaction, calculated using a binary interaction model, and with published information. Supplementary investigations of the mixing behaviour of additional blends are also reported and the results compared to model predictions. Calculations have been scaled using segmental interaction parameters derived from previous investigations of blends involving polyamides and copolyesteramides. By establishing boundary conditions for interactions in blends of polyesters and bisphenol A polycarbonate, the segmental interaction parameters involving carbonate segments have been estimated and found to be quantitatively similar to those involving the ester moiety. Results confirm that interactions in blends of polyesters and polycarbonate can be exothermic when certain compositional requirements are satisfied; however, the model predicts exclusively endothermic mixing for all binary polyester blends and that in these situations, miscibility occurs only when the entropic contribution to the free energy of mixing overwhelms the unfavourable interaction. Events that may moderate the mixing behaviour of blends, such as transesterification, have also been addressed. Exploratory projections are also presented for blends involving aliphatic polycarbonates and liquid crystalline polyesters. The results presented are broad in scope and exceptions to predictions are accounted for by considering the simplifications introduced to perform the analysis. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyesters; polycarbonates; interactions)

INTRODUCTION

Blends involving polyesters, both aliphatic and those containing aromaticity, and polycarbonates have been investigated and reviewed extensively over the preceding decades[1–30]. The focus of attention is invariably directed to the reasons for their ability to form homogeneous mixtures with themselves and a wide variety of other materials[21–23] and the exploration of the beneficial properties that may be gained by blending them[13,14,17]. More recently, considerable effort has also been directed to blends composed of liquid crystalline derivatives of polyesters[8,25–30], both as binary blends with regular polyesters and polycarbonate, respectively.

Except for some early in-depth studies[4–6] of blends of polycarbonate and aliphatic polyesters, and a more recent analysis of binary blends of aliphatic polyesters[31], inspection of the literature cited above indicates that no complete description has been proposed to account for the influence of chemical structure on miscibility. In a recent preliminary description[32] that addressed this question, a simple picture was presented of the underlying dependence for miscibility, in terms of chemical composition, in blends of polycarbonate and all polyesters.

This communication will expand upon this proposal and will also address the influence of chemical content on the fundamental phase behaviour of all binary polyester blends, including some liquid crystalline polyesters. The foundation for the analysis draws substantially from that presented in the early studies[4–6] mentioned above; however, it is also derived from information garnered from a series of investigations[33–45] attempting to correlate mixing behaviour with chemical content and structure in binary polyamide blends. Examples of this linkage, involving blends of polyamides, polyesters and their copolymers have been reported recently[41,46,47].

A notable feature of the latter blend studies included modelling the phase behaviour based upon the notion that mixing is essentially random and that the overall interaction between the polymers can be represented simply as an adduct of intra- and intermolecular segmental exchange interactions formulated in terms of elementary chemical species or mers, such as methylene and ester groups, and their respective relative abundance. Although most of the discussion of experimental data relies on information already presented in the literature, some additional studies, described below, will be included to supplement the published work and probe some of the predicted trends arising from the analysis.

THEORETICAL BACKGROUND

Previous publications[31–41,46] have presented in detail the theoretical background applied here; however, a brief summary is also provided here to complement the following arguments and discussion. The adaptation of the Flory–Huggins framework of the thermodynamics of mixing of polymers, depicted by equation (1), in the development of a binary interaction model, BIM, has proven to be a valuable tool for investigating phase behaviour of many different blends.

$$\Delta G/RT = (\phi_1/N_1 \ln \phi_1 + \phi_2/N_2 \ln \phi_2) + \chi_{12}\phi_1\phi_2 \qquad (1)$$

For a mixture of polymers 1 and 2 of mixture volume fraction ϕ, the relationship between equation (1) and the model is to express the overall interaction, χ_{12} as equivalent to χ_{Blend}, and is summarized in a convenient form as equation (2).

$$\chi_{\mathrm{Blend}} = \sum_{i,j} \psi_i^1 \psi_j^2 \chi_{ij} - \left[\sum_{i,j} \psi_i^1 \psi_j^1 \chi_{ij} + \sum_{i,j} \psi_i^2 \psi_j^2 \chi_{ij} \right] \quad (2)$$

Miscibility occurs when $\chi_{\mathrm{Blend}} < 0$; however, for blends involving polymers of moderate molecular mass, miscibility can also be obtained for positive values of χ_{Blend} but less than a critical value, χ_{Crit}, that is defined by equation (3). N is the weight-average degree of polymerization and ψ_i is the segment volume fraction.

$$\chi_{\mathrm{Crit}} = \left[N_1^{-0.5} + N_2^{-0.5}\right]^2/2 \quad (3)$$

It has been demonstrated on numerous occasions that the simple semi-empirical model can be used to develop a broad, but quantitative, description of mixing in terms of segmental interaction parameters. The segments can be defined using any convenient nomenclature; however, one scheme that has been particularly useful defines segments as elementary species, such as methylene and ester groups. Although there are advantages in applying this simple scheme, it may also introduce difficulties in the form of an increase in the number of parameters required to define the blend and uncertainties concerning the influence of configuration, i.e. nearest neighbours, on segmental interaction parameters. Provided that the latter is recognized beforehand, allowances can be made for any deviations from expected behaviour.

The concept of configuration as an influence on segmental interactions is straightforward to accept. Unfortunately, the ability to incorporate a quantitative adjustment to the model directly into equation (2), to account for the latter, is far more difficult and currently represents the most limiting feature of the model.

EXPERIMENTAL

A summary of the polymers referred to in the experimental studies reported here is presented in *Table 1*. Compositional information, in the form of segment volume fraction, ψ_i, is also given. These quantities have been derived, as described previously, using group contributions to the molar volume of polymers, ν_i. Values of ν_i, for the various segments, are also indicated in the table together with compositional information on some of the polymers central to the discussion.

The source and nature of many of the aliphatic polyesters have been documented previously[31]; however, additionally, the poly(1,4-cyclohexane dimethylene succinate) (PCDS) was obtained from Scientific Polymer Products and the poly(glycolic acid) (PGA) was obtained from Polysciences Inc. The polyester PCDACD, derived from 1,4-cyclohexanedimethanol and 1,4-cyclohexanedicarboxylic acid, was kindly provided by G. Stack of the Eastman Chemical Co.

Blends have been prepared almost exclusively in the proportion of 50:50 wt/wt by co-precipitation from a common solvent into an excess of diethyl ether acting as a non-solvent. For the blends based on either PC and PAr, respectively, with the aliphatic polyesters, chloroform was used as the solvent. Blends based upon the semi-aromatic polyesters, e.g. PBT, were prepared using hexafluoroisopropanol as the solvent. The PC/PGA blend was dissolved using a heated mixture of phenol and 1,1,2,2-tetrachloroethane (*ca.* 3:2 v/v). Exposure to this solvent was minimized to prevent significant degradation of the PGA.

Thermal analysis was applied using a Perkin-Elmer Series 7 differential scanning calorimeter at a heating rate of either 10 or 20°C min^{-1}. Optical microscopy, using a Nikon Microphot-FX operating with cross-polarizers and a Polaroid camera, was also used to assist elucidation of phase behaviour.

DISCUSSION

Polyester–polycarbonate blends

Blends of aliphatic polyesters and bisphenol A polycarbonate. Subsequent to the early studies, conducted by Paul, Barlow and co-workers[4–6, 22, 23], very little new information has been published concerning the influence of chemical structure on the phase behaviour of aliphatic polyester/polycarbonate (PC) blends. From these investigations, it was concluded that miscibility occurs when the methylene content of the polyester is approximately

Table 1 Summary of composition and properties of polymers

Polymer	Composition (segment volume fraction)[a]					
	T_g (°C)	T_m (°C)	Ψ_A	Ψ_C	Ψ_D	Ψ_F
PGA, poly(glycolic acid)	32	220	0.4007	–	0.5993	–
PCDS, poly(cyclohexane dimethanol succinate)	– 3	118	0.7574	–	0.2426	–
PCACD	53	200	0.8091	–	0.1909	–
PEA, poly(ethylene adipate)	– 46	52	0.6673	–	0.3327	–
PBA, poly(butylene adipate)	– 64	na	0.7279	–	0.2721	–
PTMG, poly(trimethyl glutarate)	– 56	40	0.6673	–	0.3327	–
PEZ, poly(ethylene azeleate)	– 54	37	0.7506	–	0.2494	–
PET			0.2293	0.4279	0.3429	–
PBT (Valox 325)	45	226	0.3730	0.3481	0.2789	–
PAr (Ardel D100)[b]	185	–	0.1774	0.6492	0.1734	–
PCHT/I (Kodar A150)[b]	86	260	0.5170	0.2681	0.2149	–
PC (Lexan 141)	147	–	0.2441	0.5954	–	0.1605

[a] Calculated using $\nu_A = 16.45$ ($-CH_2-$), 50.35 ($-C(CH_3)_2-$), 87.8 $\mathrm{cm^3\,mol^{-1}}$ ($-C_6H_{10}-$); $\nu_B = 24.9\ \mathrm{cm^3\,mol^{-1}}$; $\nu_C = 61.4\ \mathrm{cm^3\,mol^{-1}}$; $\nu_D = 24.6\ \mathrm{cm^3\,mol^{-1}}$; $\nu_F = 33.1\ \mathrm{cm^3\,mol^{-1}}$

[b] Contains a mixture of 1,4- and 1,3-isomers of phthalic acid (approx 2:1 molar ratio)

between two and seven methylene segments per ester group. Branching, in the form of methyl groups close to the ester group was found to have an adverse influence on miscibility[6]. Calorimetric studies[22, 23], on mixing of small molecular analogues, also supported the inference that an exothermic interaction drives homogeneous mixing in blends with the linear polyesters.

The latter observations represent an important contribution to the calculations and arguments developed here; however, the main purpose of the discussion in this section is to review the requirements for miscibility in blends of linear polyesters with PC in order to establish the critical limits of polyester composition, where $\chi_{\text{Blend}} = 0$. For example, it had always been assumed that a blend of PC and the polyester comprised of only one methylene per ester group, poly(glycolic acid) (PGA), is immiscible; a reasonable assumption that appears not to have been investigated. Thermograms shown in *Figure 1*, where the PC/PGA blend exhibits two T_gs, commensurate with those of the pure constituents, support the expected behaviour. Additionally, there is no appreciable retardation of the rate of crystallization of the PGA in the blend and quenching from the melt fails to vitrify the mixture.

Polyesters containing alicyclic structures may also be expected to behave like aliphatic polyesters. Thermograms presented in *Figure 2* and *Figure 3* confirm the miscibility of PC with the cyclic polyesters PCDS[48] and PCDACD[49], respectively. For the blend based on PCDS, the initial thermogram (*Figure 2a*) of the as-prepared blend illustrates that both the polyester and PC have developed significant crystallinity. Both PCDS and PCDACD are easily vitrified from the melt (*Figure 2d* and *Figure 3a*) to yield essentially amorphous polymers. The presence of the miscible PC, and the concomitant increase of T_g relative to the pure polyester, will retard the rate of crystallization even further. Hence both blends, when exposed to temperatures above the highest melting component then quenched in liquid nitrogen, exhibit a single T_g (*Figure 2b* and *Figure 3b*) intermediate between the two components.

In PC/PCACD, the higher blend T_g ($\approx 91°C$), compared to the blend with PCDS ($T_g = 40°C$), precludes crystallization of the PC[50]. Melting of the crystallized polyester, by exposure to 220°C for 1 min followed by quenching, is sufficient to illustrate complete miscibility.

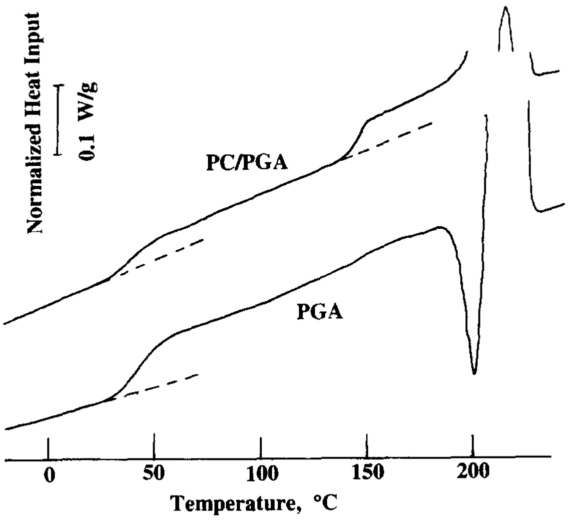

Figure 1 D.s.c. thermograms of poly(glycolic acid) (PGA) ($-CH_2COO-$) and a 50:50 PC/PGA blend. Both quench-cooled from the melt (240°C)

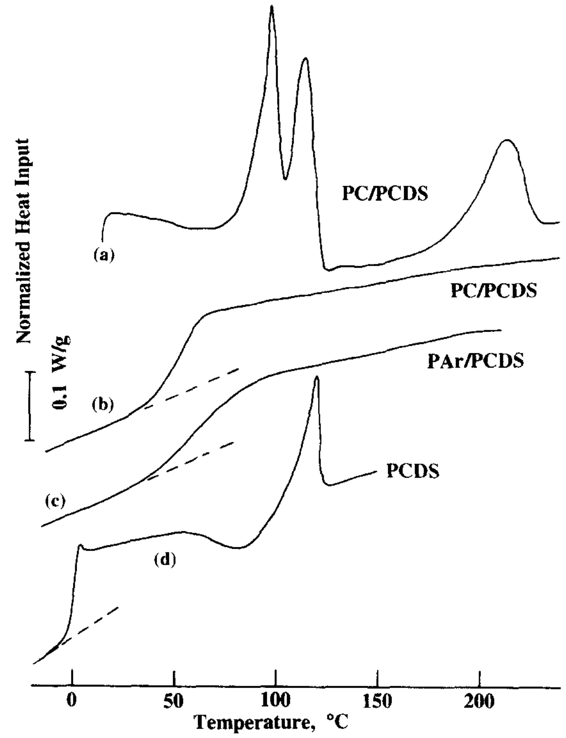

Figure 2 Representative thermograms of blends (50:50) of PC and PAr, based on PCDS: (a) as prepared; (b,c) quenched in liquid nitrogen from the melt (245°C for 1 min); (d) pure PCDS quench-cooled from the melt (160°C)

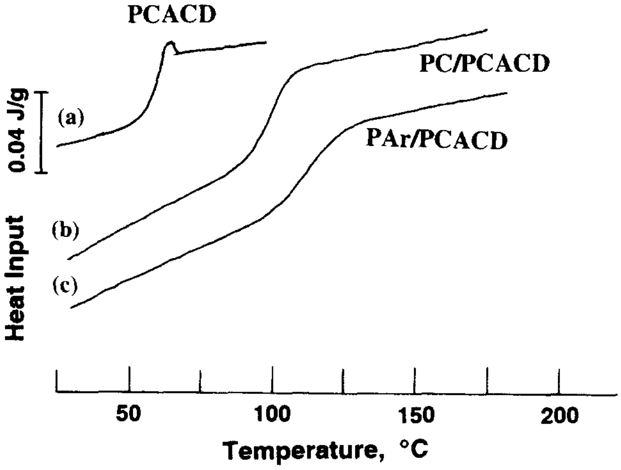

Figure 3 D.s.c. thermograms of (a) pure PCACD and (b) blends (50:50) of PC (b) and PAr (c), based on PCACD

It is also instructive to compare the measured blend T_gs, noted above, with the respective values calculated using equation (4). In a miscible blend of polymers 1 and 2, where x is the mass fraction and ΔC_p is the incremental heat capacity at T_g, the mixture $T_{g1,2}$ is given by[51]:

$$\ln T_{g1,2} = \frac{x_1 \Delta C_{p1} \ln T_{g1} + x_2 \Delta C_{p2} \ln T_{g2}}{x_1 \Delta C_{p1} + x_2 \Delta C_{p2}} \qquad (4)$$

For PC (measured here as $\Delta C_p = 0.266\ \mathrm{J\,g^{-1}\,K^{-1}}$; $T_g = 420\ \mathrm{K}$) in a 50:50 (w/w) blend with PCDS (measured here as ($\Delta C_p = 0.392\ \mathrm{J\,g^{-1}\,K^{-1}}$; $T_g = 270\ \mathrm{K}$), equation (4) gives a calculated T_g of 50°C (compared with a measured value of 40°C). Similarly, for PC in a 50:50 (w/w) blend with PCACD (measured here as $\Delta C_p = 0.205\ \mathrm{J\,g^{-1}\,K^{-1}}$; $T_g = 326\ \mathrm{K}$), equation (4) gives a calculated T_g of 103°C (measured as 91°C).

The approximate 10°C overestimation in both cases is typical for transition temperatures measured at the onset and is indicative of a broadened transition region. However, it is noteworthy that the analysis provides results that are consistent with the fact that the ΔC_p of PCACD is almost half of that measured for PCDS. The results obtained from equation (4) are sensitive to values of ΔC_p and in blends where the lower T_g component has a large ΔC_p relative to the other component, a strong negative deviation from linearity between the T_gs of the pure components is predicted. Accordingly, in the context of equation (4), the relatively large ΔC_p of aliphatic polyesters provides a rational explanation of their strong plasticizing action on PC. Although PCACD is an exception to this trend, the circumstances noted above will apply to most miscible PC/aliphatic polyester blends.

Additional examples of miscible blends of PC, with poly(butylene adipate) (PBA) and poly(ethylene azaleate) (PEZ) respectively, are presented in *Figure 4*. The phase behaviour of the PC/PEZ blend does not yet appear to have been described in the literature. The PC/PBA blend has a broad onset T_g at -17°C (*Figure 4a*). Although this appears to be rather low, a calculation using equation (4) (PBA: $\Delta C_p = 0.45\ \mathrm{J\,g^{-1}\,K^{-1}}$; $T_g = 209$ K) indicates a theoretical $T_g = -2$°C. Additional observations that support miscibility include the absence of any strong crystallization of the PBA during heating. Vitrified PBA exhibits a strong crystallization exotherm[31].

At a blend composition chosen to suppress crystallization of the polyester component (and apparently the PC), the thermogram of the miscible blend (*Figure 4b*) of only 25 wt% of PEZ (4.5 methylene groups per ester segment) causes the T_g of PC to be reduced by approximately 100°C. Conversely, the PC/PTMG (three methylene groups per ester) blend, displays substantial phase separation (*Figure 4c*). The latter blend also appears not to have been reported in the literature. In this case, the T_g of the PC is slightly depressed (125°C); however, given the rather low molecular mass of the PTMG[31] it must be concluded that the interaction between PC and the polyester containing three methylene groups per ester group is positive; at least at the reference temperature in question.

Poly(ethylene adipate) (PEA) also contains the same methylene to ester segment ratio as PTMG. Moreover, the two polymers share exactly the species when examined in terms of triad configurations of segments. There are also indications that the blend PC/PEA is also phase separated; however, because of the propensity of PEA to crystallize in the blend, there is less certainty concerning actual phase behaviour. Blends of PC/PEA, when cast as a film from a common solvent on a hot plate, to prevent crystallization of the components, provided opaque films. Similar preparation of PC/PBA blends, determined above to be miscible, gave a transparent film. Opaque films of PC/PEA only became clear at temperatures in excess of 240°C. Optical microscopy of a precipitated blend of PC/PEA revealed a grossly phase-separated mixture with a stable solid phase engulfed in a liquid phase. Separate crystallization of the liquid phase produced the detailed spherulitic morphology of the aliphatic polyester.

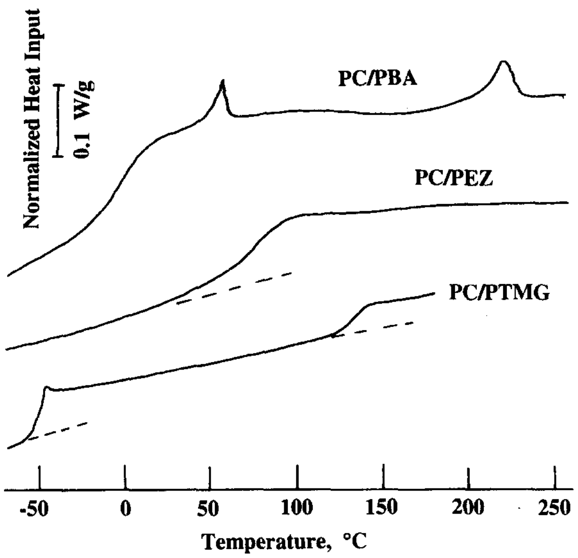

Figure 4 D.s.c. thermograms of blends (50:50) of PC and PBA, PEZ and PTMG, respectively, all quenched in liquid nitrogen from the melt (250°C)

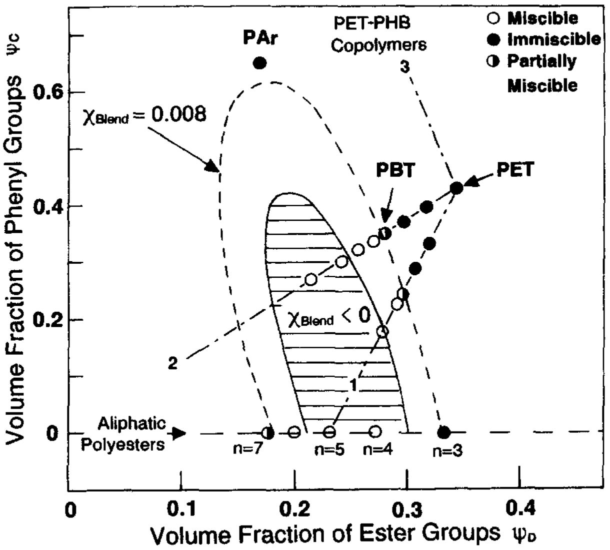

Figure 5 Comparison of experimental data of phase behaviour of blends of bisphenol A polycarbonate with aliphatic ($-(CH_2)_nCOO-$) and semi-aromatic polyesters with binary interaction model calculations using segmental interaction parameters in *Table 2*. Shaded area is where $\chi_{\mathrm{Blend}} < 0$. The broken lines (1–3) represent the locus of composition of copolyesters of PCL–PET, semi-aromatic polyesters and copolyesters $-OCO$ Phenyl $COO-(CH_2)_m-$ and PET–PHB copolymers, respectively

The behaviour described above suggests that either an upper critical solution temperature is present or perhaps rapid transreaction induced miscibility occurs. The latter explanation is supported by n.m.r. analysis of a sample exposed to 260°C for 1 min that indicated a significant degree of transreaction between the components. Accordingly, it must be concluded that the latter presents further evidence that at the reference temperature of approximately 235°C, blends of PC and aliphatic polyesters containing three methylene segments per ester group are immiscible. This inference is contrary to that proposed earlier.

For the purposes of the arguments developed here, and in view of the foregoing, the critical limits for miscibility in PC/aliphatic polyester blends, where $\chi_{\mathrm{Blend}} = 0$, is somewhere between seven and three methylenes per ester group. Thus using the formalism and procedures described in previous publications, interactional null points have been established for volume fraction of methylene groups in the polyester A_yD_{1-y}, at $\psi_A = 0.70$ and 0.79, respectively. The definition of A as methylene groups can also be extended to alkyl-type species, such as methyl and cyclohexyl moieties, provided the appropriate respective contributions to molar volume are included.

All of the information discussed above is summarized qualitatively in *Figure 5*. In order to propose a quantitative fit of the model to the data, also shown in the figure, the χ_{ij} associated with the interactions of the carbonate group are required, as will be detailed below.

Blends of semi-aromatic polyesters and bisphenol A polycarbonate. The question of (im)miscibility in blends of PET and PC appears to have been resolved some time ago[11]. Subsequent studies[7,8] have strived to confirm and qualify the heterogeneous nature of this blend. Moreover, there are indications[12] that the interaction between these two polymers is substantially unfavourable. Similar investigations involving PBT have been somewhat more controversial owing primarily to the ability of transesterification and crystallizability to obscure the true nature of the phase behaviour; however, it is clear that the latter also has an unfavourable interaction with PC, but in this case forms a partially miscible system[52,53].

For these reasons the behaviour of PBT/PC has been chosen to provide a boundary condition where $\chi_{\mathrm{Blend}} = 0.01$. A similar value has been reported previously[54]; however, the authors use a different reference volume than that applied here ($V_{\mathrm{ref}} = 100\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ [48]).

Solving the three simultaneous equations, established using the values of χ_{Blend} for the systems described above and recorded values for χ_{AD}, χ_{AC} and χ_{CD} shown in *Table 2*, provides a quantitative evaluation of the unknown segmental interaction parameters involving carbonate segments; χ_{AF}, χ_{CF} and χ_{DF}. Summarized in *Table 2*, there are several features concerning the data shown that are qualitatively consistent and worthy of discussion.

First, all values are positive indicating an unfavourable exchange interaction. As may be expected, the close similarity of structure and content of ester and carbonate groups provides similar values of their interaction with the same species. In addition, the interaction between ester and carbonate groups themselves is sensibly relatively small.

A pictorial representation of the behaviour of χ_{Blend}, as provided by the parameters given in *Table 2*, for blends of PC with all polyesters that can be defined as ACD polymers is given in *Figure 5*. The figure makes no allowances for isomerism, e.g. phenyl group isomers, or the effects of configuration of segments on their respective interactions. Both of these structural factors are known to influence interactions[38,39], thus distortions of the calculated behaviour for some polymer blends, when compared to actual behaviour, should be anticipated.

In the region where $\chi_{\mathrm{Blend}} < 0$, the calculated values of χ_{Blend} for the miscible PC/aliphatic polyester blends are only slightly negative with the minimum at approximately $\chi_{\mathrm{Blend}} = -0.004$. Second, *Figure 5* illustrates how the rather strong unfavourable interaction between PC and PET ($\chi_{\mathrm{Blend}} = 0.05$), alluded to above, arises. The extended line (2) drawn through PBT and PET defines the locus of composition of polyesters –OCO Phenyl COO–$(CH_2)_m$– and on this locus the phase behaviour is marked of additional blends of PC with copolyesters obtained from the literature[3,55–57]. In some of the data points given, the blends involved polyesters containing cyclohexyl structures and mixed isomers, 1,4- and 1,3-, of the phenyl group. In all cases, the cyclohexyl group has been rationalized as an ensemble of methylene groups.

Table 2 Values of segmental interaction parameters

Segments	Segmental interaction parameter, $\chi_{i,j}$	Value
$-CH_2-/-C_6H_4-$	$\chi_{\mathrm{AC}}{}^{a}$	0.1
$-CH_2-/-CO\ O-$	$\chi_{\mathrm{AD}}{}^{a}$	2.23(3)
$-CH_2-/-O\ CO\ O-$	χ_{AF}	2.78(1)
$-C_6H_4-/-CO\ O-$	$\chi_{\mathrm{CD}}{}^{a}$	1.69(2)
$-C_6H_4-/-O\ CO\ O-$	χ_{CF}	2.52(9)
$-CO\ O-/-O\ CO\ O-$	χ_{DF}	0.29(6)

[a] From refs [41,46]

The calculations indicate a window of complete miscibility, when $\chi_{\mathrm{Blend}} < 0$, for values of m between approximately 6 and 10. This window would narrow considerably if the boundary condition provided by PC/PBT as $\chi_{\mathrm{Blend}} = 0.01$ is an underestimation. Conversely, a larger effective miscibility window may be anticipated if the molecular weight of the blend constituents is not too large. Hence the locus of $\chi_{\mathrm{Blend}} = 0.008$ is also given in the figure to indicate a sensible upper limit for miscibility that includes those blends where miscibility is driven by the entropic contribution to the free energy of mixing. Investigations[58] of blends of PC and semi-aromatic polyesters with values of $m = 7$ and 9, respectively, indicated that co-precipitated blends were miscible; a result in agreement with the information presented in *Figure 5*. However, solution-cast blends were found to be phase separated. Although transreaction between the components was speculated to be a factor contributing to miscibility, it may also be concluded that the $\Delta\chi$ effect is the more likely cause for the observed immiscibility in the blends.

Also noted in the figure is the locus of composition of PCL/PET copolymers and data obtained from studies[59–61] of the phase behaviour of blends of the latter with PC. Although the authors concluded that the phase behaviour observed could not be predicted by a Flory–Huggins theoretical approach, it is apparent from the results presented here that not only is the theory appropriate to these blends but also that the level of agreement is quite good.

The commercial availability of the aromatic polyester polyarylate (PAr) has promoted a number of studies involving blends with PC. The extension of the analysis, and the associated segmental interaction parameters, to this blend leads to a calculated value of $\chi_{\mathrm{Blend}} = 0.011$ and supports the expectation of a heterogeneous blend that may easily become miscible in the presence of a small amount of transreaction.

The locus of composition of PET–PHB copolymers, shown in *Figure 5*, illustrates an increasingly unfavourable interaction with PC as the PHB content increases. A recent review[9] of reported behaviour supports this general result; however, the relatively high melt processing required to evaluate blends of PC with these copolymers, and the associated consequences of transesterification, also leads to some potentially erroneous conclusions of (partial) miscibility. It is important to note here, and also with regard to discussions presented below, that as the configurational content of the segments in a polymer departs strongly from that of the polymers in which the segmental interactions were determined, there is a greater probability of significant deviations from predicted behaviour[40].

Blends of polyesters and aliphatic polycarbonates. Interest in blends of aliphatic polycarbonates has been much less than that of the aromatic polycarbonates, such

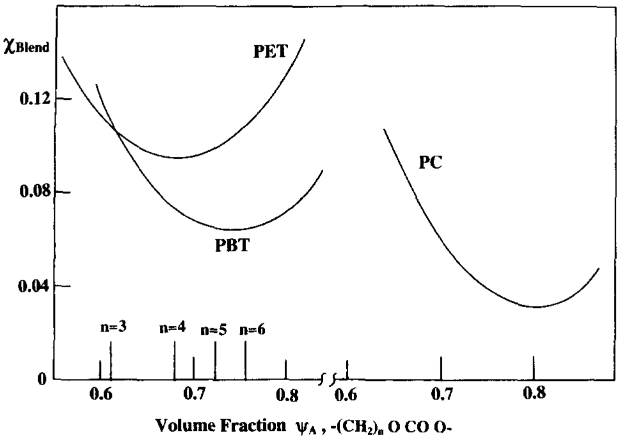

Figure 6 Calculated values of $\chi_{\rm Blend}$ for semi-aromatic polyesters, PET and PBT, and bisphenol A polycarbonate, respectively, in aliphatic polycarbonates

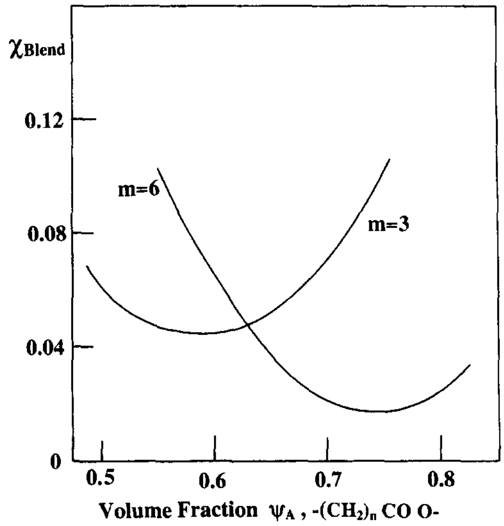

Figure 7 Calculated values of $\chi_{\rm Blend}$ for aliphatic polycarbonates $-(\rm CH_2)_{\it m}$ O CO O–, in aliphatic polyesters

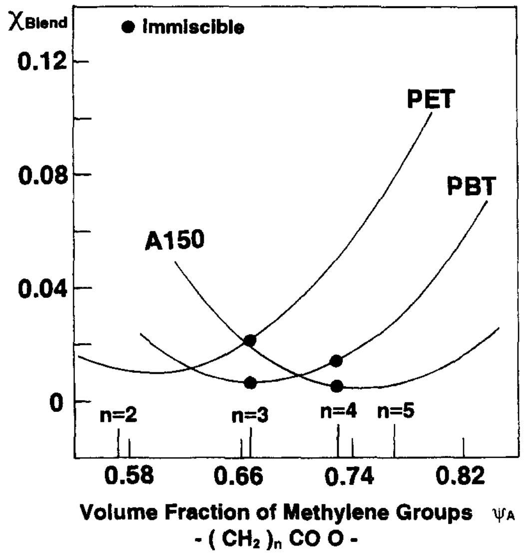

Figure 8 Comparison of calculated values of $\chi_{\rm Blend}$, obtained using parameters in *Table 2*, with experimental behaviour reported in *Table 3* and the literature (refs [69,70]), for blends of aliphatic polyesters and PET, PBT and a copolyester (Kodar A150), respectively

as those based on bisphenol A. Polyurethane elastomers represent one area of practical interest where aliphatic polycarbonates have been incorporated into blend studies with PC[62]. The parameters given in *Table 2* also allow some exploratory calculations of interactions in blends involving aliphatic polycarbonates with aliphatic and semi-aromatic polyesters, respectively. Shown schematically in *Figure 6* and *Figure 7* the results presented also show calculated values of $\chi_{\rm Blend}$ of bisphenol A PC in aliphatic polycarbonates. In all cases calculations indicate a strongly unfavourable interaction with the expectation of heterogeneous mixtures. Recently published experimental information[63], indicating phase separation in a block copolymer of PCL and poly(trimethylene polycarbonate), provides some support for the projections shown in *Figure 7*.

Binary blends of polyesters

Both the experimental and theoretical aspects of binary aliphatic polyester blends have been addressed in the literature[64–66]. For blends $\rm A_yD_{1-y}/A_xD_{1-x}$, mixing is exclusively endothermic, but because of the relatively small ester–methylene interaction, these blends can tolerate a relatively large dissimilarity of alkyl content before the entropically driven miscibility is overcome by the unfavourable enthalpic interaction[32].

When the alkyl content difference of the polyesters becomes sufficiently large, a heterogeneous blend is obtained[67,68]. The blend PCDS/PCACD (calculated $\chi_{\rm Blend} = 0.006$) appears to be close to the criterion for (partial) miscibility. Thermal analysis of the blend indicated that although the T_g of the PCDS is relatively unaffected, the T_g of the PCACD component is reduced and broadened considerably. Perhaps indicative of some partial miscibility, PCDS and PCACD are essentially immiscible. It is apparent that the rationalization of cyclohexyl structures as an ensemble of methylene groups may be an oversimplification in this instance.

The small changes of segmental interaction parameters that may be associated with cyclohexyl segments are presumably insufficient to cause observable deviations in expected behaviour in those blends, such as PC/PCDACD, where failure to distinguish between the different alkyl segments appears inconsequential.

Aliphatic/semi-aromatic. Extending the analysis to binary blends of aliphatic polyesters with semi-aromatic polyesters produces the information shown in *Figure 8*. The experimental data points have been extracted from the literature [71,72] and separate studies conducted here summarized in *Table 3*. The predicted trends show that $\chi_{\rm Blend}$ is always positive, with no athermal condition, and unfavourable for homogeneous mixing. Although the experimental data support this result, entropically driven miscibility may be expected as the alkyl (methylene) content of both components increase.

A blend of the copolyester Kodar A150 and poly(butylene adipate) represents an example where $\chi_{\rm Blend}$ (≈ 0.005) is predicted to be close to zero and where entropically driven miscibility may be expected to occur; however, thermograms shown in *Figure 9* illustrate the formation of an immiscible blend which appears to undergo some homogenization, presumably due to transreaction, upon exposure to higher temperature.

The ability of cyclohexyl units to confound some

Table 3 Thermal properties and phase behaviour of blends of aliphatic polyesters with aromatic polyesters

		PBT ($T_g = 45°C$)		Kodar A150 ($T_g = 86°C$)	
Aliphatic polyester (T_g°C)	CH_2/COO	T_g(°C)	Phase behaviour	T_g(°C)	Phase behaviour
Poly(trimelthylene glutarate) (− 56)	3	− 57, no	I	–	–
Poly(butylene adipate) (− 64)	4	–	–	− 61, 70	I
Poly(ethylene adipate) (− 46)	3	− 49, no	I	–	–

no = not observed (obscured by aliphatic polyester melting)

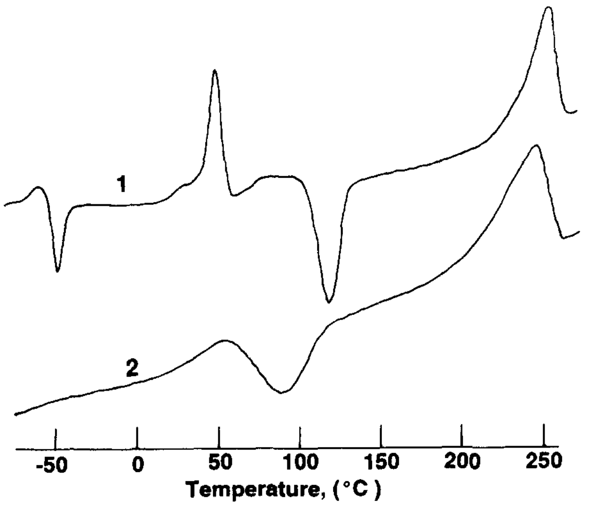

Figure 9 Thermograms of the blend PBA and copolyester Kodar A150 (50:50) quench-cooled from the melt at 290°C for (1) 1 min and (2) 3 min

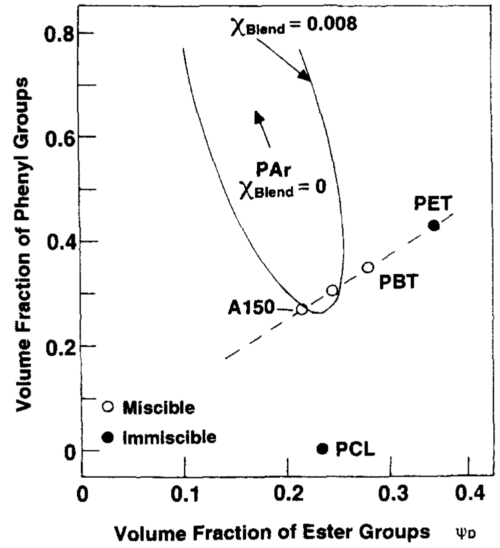

Figure 10 Comparison of experimental phase behaviour and calculated values of χ_{Blend} of blends of polyarylate and polyesters. The broken line represents the locus of composition of semi-aromatic polyesters and copolyesters –OCO Phenyl COO–$(CH_2)_m$–

expected behaviour has already been alluded to above and the latter blend presents an additional example of such behaviour.

A distinctly more favourable comparison of experimental data with calculations is provided by reported behaviour of blends of PBT–PCL random copolymers with PCL[73]. *Figure 8* indicates the blend PBT/PCL to have a significant unfavourable interaction ($\chi_{Blend} = 0.028$) for homogeneous mixing. As the amount of PBT copolymerized with PCL is decreased, the interaction of the copolymer with pure PCL will diminish to zero. Calculated values of χ_{Blend} of 0.017, 0.009 and 0.005 for blends of PCL with copolymers containing 80, 60 and 46 wt%, respectively, of PBT indicates that entropically driven miscibility would be expected to occur when the copolymer contains below 60 wt% PBT; a result in accordance with the conclusions of the authors.

Finally, it has been reported that PAr forms immiscible mixtures with PCL[74]. Separate studies undertaken here, but not reported in detail, have confirmed this behaviour. It is perhaps unexpected that PC and PAr behave in a contradictory way with regard to phase behaviour in blends with PCL; however, in the following section a sensible explanation can be proposed.

Semi-aromatic/semi-aromatic. Polyarylates have attracted considerable attention in blend studies, most notably with PET and PBT, respectively. Although transesterification can occur quite easily it is concluded that PAr is immiscible with PET[9,19] and miscible with PBT[9,75]. Copolyesters based on PET with cyclohexyl dimethanol have also been reported to be miscible with PAr[10,76]. Currently, no universal picture has been presented that captures the essential thermodynamics of this behaviour and that discussed in the previous section involving PCL.

Calculations, presented in *Figure 10*, represent a first-order approximation towards this objective. The locus of $\chi_{Blend} = 0.008$ is shown to define loosely an expected region of entropically driven miscibility. Although the miscible blends involving PBT ($\chi_{Blend} = 0.013$) and the copolyester Kodar A150 ($\chi_{Blend} = 0.008$), are close to the boundary, the figure promotes a perception of why miscibility can occur with polyesters in this range of composition. Note that the prediction of an unfavourable interaction, and hence heterogeneous mixing, of PAr with PET ($\chi_{Blend} = 0.045$) and PCL ($\chi_{Blend} = 0.026$), respectively, is supported by the experimental data. Indeed, the figure indicates that all aliphatic polyesters will be immiscible with PAr; however, the thermograms in *Figures 2 and 3* illustrate that both PCDS and PCACD form miscible blends with PAr[49]. Once again, by rationalizing the latter as aliphatic polyesters, the presence of cyclohexyl groups introduces a deviation from expected behaviour. There appears to have been no systematic investigation of phase behaviour of blends of PAr with other linear aliphatic polyesters.

Phase behaviour of binary blends of homologous semi-aromatic polyesters and copolyesters, such as PET and PBT, can be summarized schematically as shown in *Figure 11*. The calculations are centred on PBT, but similar results are obtained irrespective of the polyester.

Investigations of PET/PBT blends have reported differing opinions concerning phase behaviour[9,75–77]. A calculated value of $\chi_{Blend} = 0.013$, given here, suggests partial miscibility or complete immiscibility may occur with a

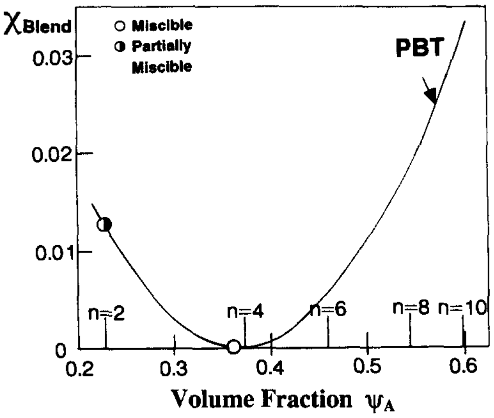

Figure 11 Calculated values of χ_{Blend}, obtained using parameters in *Table 2*, for binary blends of semi-aromatic polyesters –OCO Phenyl COO–(CH$_2$)$_n$– centred on PBT ($n = 4$; $\chi_{Blend} = 0$), as a function of methylene content

sensitivity to molecular mass. Nevertheless, the potential for rapid transreaction, known to occur in these blends[78], is provided for by the marginally unfavourable interaction. As the difference of methylene content of the polyesters becomes smaller, entropically driven miscibility is expected to be more likely to occur. Accordingly, a blend of PBT and a copolyester of similar methylene content ($\psi_A = 0.36$; compare with $\psi_A = 0.373$ for PBT), and with a calculated value of $\chi_{Blend} \approx 0$ has been reported[79] to be miscible (see *Figure 11*).

The authors of the latter study also conclude that blends of PET and the same copolyester are miscible[80], because of favourable entropic effects that overcome a small endothermic interaction. Calculations based on the information here indicate that $\chi_{Blend} \approx 0.01$ for the latter blend and that χ_{Blend} increases in blends of PET and copolyesters of PET containing cyclohexyl dimethanol. Accordingly, the blend PET/Kodar A150 has a rather strong unfavourable interaction for homogeneous mixing ($\chi_{Blend} = 0.05$). The imminent widespread commercial availability of poly(propylene terephthalate) (PPT) suggests that blends of PPT/PET and PPT/PBT will attract some attention in the near future. Calculations indicate only slightly unfavourable interactions (0.004 and 0.003, respectively) and a prognosis for miscibility.

Although it is known that in blends involving polyamides interactions are affected slightly by phenyl group isomerism, it is anticipated that it would not be sufficient to cause phase separation in a blend where the isomeric composition represents the only difference between the constituents. For example, a blend of PET and its isomeric analogue PEI would be expected to be completely miscible. There is some support[81] for the latter assumption. Additionally, replacement of a phenyl group by a polycyclic group, such as in naphthalene-based polyesters, would be expected to behave in an analogous way to the semi-aromatic polyesters. Accordingly, studies[82] of PEN/PBN blends (N = naphthalate) have indicated partial miscibility similar to that concluded for PET/PBT blends. Without any clear knowledge of the interactions involving the naphthalene segment, the latter discussion is somewhat speculative; however, the framework from which to address this question is clearly in place.

CONCLUSIONS

From the discussion above, it is possible to highlight several distinct new developments concerning blends of polyesters and polycarbonates. First, a critical evaluation of phase behaviour and interactions in blends of aliphatic and semi-aromatic polyesters, respectively, with bisphenol A polycarbonate has been presented in the context of a binary interaction model. This represents the first such treatment that attempts to include both aliphatic and aromatic elements of chemical structures. It has been proposed that the window of miscibility, defined by an exothermic interaction, in blends of bisphenol A polycarbonate and linear aliphatic polyesters should be slightly smaller than has been suggested in the past; however, the modification remains tentative and further experimental studies, perhaps involving aliphatic copolyesters with a low proclivity to crystallize, may help to resolve some of the remaining uncertainties.

A second, and significant, outcome of the analysis includes a determination of the segmental interactions involving carbonate segments with simple chemical structures, such as methylene groups, and their application to provide an initial estimation of interactions in blends of polyesters and aliphatic polycarbonates. Additionally, it has been found that the trend of the magnitude of the interactions of the carbonate group with other species is consistent with those obtained for the ester group.

Finally, in all binary blends involving polyesters, both aliphatic and semi-aromatic, that are defined in terms of A, C and D segments the model predicts exclusively endothermic mixing. This conclusion is an extension to that proposed earlier for binary aliphatic polyester blends. Accordingly, miscibility occurs only when the entropic contribution to the free energy of mixing is capable of overcoming an unfavourable interaction. For polyesters, the latter condition may occur more frequently than anticipated owing to the usually low molecular mass of this class of condensation polymer.

The level of agreement between model predictions and experimental behaviour is quite good, especially when the simplifications and approximations required to perform the analyses are taken into consideration. This task has been complicated further by the fact that miscibility in many of the types of blends addressed here is projected to occur exclusively owing to a favourable entropic contribution to the free energy of mixing that is sufficient to overwhelm the unfavourable interaction. Notable exceptions to model predictions have been identified and probable causes discussed in terms of discrepancies attributed to over-simplification of some of the chemical structures of the polymers. For example, the treatment of cyclohexyl structures, as a collection of methylene segments whose interactions are quantitatively equivalent, appears to be sufficient for the interpretation of blends involving semi-aromatic polyesters but not for the aliphatic polyesters that contain them. Although the quantitative nature of the interactions calculated between the various polymers should be considered approximate, the underlying qualitative trends in the changes of the predicted interaction, with changes in chemical composition, should be regarded as more meaningful.

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