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Phase behaviour of polyamide–polyester blends: the influence of aromaticity

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Miscibility in blends of semi-aromatic polyamides and random aliphatic co-polyesteramides, derived from ϵ-caprolactam, ϵ-caprolactone and laurolactam has been investigated by calorimetric methods. Dilution of ϵ-caprolactam by ϵ-caprolactone in PA-6 transforms miscible blends based on PA-6I and PA-TMDT, respectively, to immiscible mixtures at approximately 35 and 46 mol%, respectively, of ϵ-caprolactone in the copolymer. The data have been found to conform to an analysis provided by a binary interaction model incorporating segmental interaction parameters, χ_{ij}, derived from related blends. Extension of the treatment to polyamide/polyester blends whose constituents contain aromaticity, e.g. PA-66/poly(ethylene terephthalate), PET and PA-6I/polyarylate, PAr, has also been explored. The results confirm the gross immiscibility, indicated by a large unfavourable interaction parameter, typically encountered in these blends. © 1997 Elsevier Science Ltd.

(Keywords: polyamides–polyester copolymers; miscibility; interactions)

INTRODUCTION

In an earlier publication[1], the phase behaviour of blends of aliphatic polyamides, polyesters and their copolymers was interpreted using a binary interaction model, BIM, which was then used to derive an estimate of the segmental interactions involved. A significant outcome of the analysis was the assertion that homogeneous mixing could only occur when the combinatorial entropy of mixing overcomes an exclusively unfavourable interaction. Subsequent investigations of related polymer blends[2–5] have indicated that the parameters derived can be applied successfully to different blend situations. As part of an ongoing effort to extend this kind of treatment to additional systems, the next step is to establish the mixing relationships in polyamide-polyester blends whose components contain aromaticity, e.g. PET.

The blending of aliphatic polyamides and polyesters, such as PA-66 and poly(ethylene terephthalate), PET, has been investigated on numerous occasions[6–11] indicating the formation of phase separated mixtures with poor interfacial adhesion. Attempts to remedy this by promoting chemical interchange between ester and amide groups during melt processing have also been explored[8,11]. It is reasoned that the formation of copolymers resulting from such reactions will promote better dispersion and adhesion at the interface and improve mechanical strength. Transreaction between polymers in the melt, although dependent upon chemical factors, is also related to the degree of mixing in the interfacial regions of the two components. Accordingly, when these considerations are judged in relation to the ability of polyamide and polyester blends, respectively, to transreact during processing[12–15], it may be concluded that the degree of mixing at the interface between PA-66 and PET is extremely small.

Within a conventional treatment of the thermodynamics of polymer blends the situation described above can be characterized as a highly unfavourable interaction between the components, i.e. χ the Flory–Huggins interaction parameter, is strongly positive. The foregoing, although representative of a first approximation, exemplifies current thought concerning mixtures of these polymers.

Assessing the magnitude of the interaction between polymers such as these is important, because it would allow for chemical manipulation, perhaps by copolymerization, in order to effect compatibilization strategies. However, an immediate obstacle is that it is extremely difficult to measure interaction parameters in immiscible systems. The fact that miscibility in blends of the latter is uncommon presents some difficulty in choosing an appropriate strategy[5] for the selection of suitable copolymers from which to define the mixing relationships. For polyamide–polyester blends, containing aromatic segments, much of the information required to perform these calculations, using a BIM, is already available. Additionally, by using the known[16–18] miscibility of polycaprolactam (PA-6) and semi-aromatic polyamides, such as poly(hexamethylene isophthalamide), PA-6I, it should be straightforward to obtain an estimate of the currently unknown phenyl–ester segmental interaction in blends of the latter with aliphatic co-polyesteramides. In this paper one particular strategy towards this objective will be illustrated. It will be shown that the principle trends predicted are both consistent with the observations documented here and experimental data presented in the literature. Some of the projections are crude and approximate; nevertheless, there is a great deal of corroborating data to imply that this broadly painted picture captures the essential elements of actual behaviour.

EXPERIMENTAL

Materials

The semi-aromatic polyamides PA-6I (poly(hexamethylene isophthalamide)), PA-TMDT (poly-2,2,4-trimethyl-hexamethylene terephthalamide) and PA-6I/6T (polyhexamethylene iso-co-terephthalamide), used in the blend studies described here, have been characterized and documented previously[16,17]. A summary of these and all the polymers involved in blends studies referred to here is provided in *Tables 1* and *2*. The nomenclature shown denotes A as alkyl groups (CH_2), B as amide groups (NHCO), C as phenyl groups (C_6H_4) and D as ester groups (COO). The volume fraction (ψ_i) has been calculated as described previously[17]. Random co-polyesteramides derived from caprolactam (LA), caprolactone (LO) and laurolactam (LL) are the same as those described previously[1,2,4].

Procedures

All blends were formulated at 50/50 (w/w) composition and were prepared by co-precipitation from a common solvent trifluoroethanol/chloroform (3/2, v/v) into a large excess of non-solvent (diethyl ether). All blends and pure materials were dried extensively under vacuum at 60°C prior to analysis. Determination of thermal properties and phase behaviour was performed using a Perkin-Elmer Series Seven differential scanning calorimeter (d.s.c.) operated at a heating rate of either 10° or 20°C min^{-1}. All blends involving crystallizable polymers were exposed to a temperature above the melting point of the latter for a short period, 1–2 min, in order to establish liquid–liquid equilibrium. Thermal analysis was conducted whenever possible on vitrified blends, formed by quenching the melt in liquid nitrogen, and all results and inferences were obtained on these samples unless noted otherwise. A single T_g, intermediate between those of the two components was used as an indication of miscibility. A strong retardation of the rate of crystallization, inferred qualitatively during thermal analysis, was also a supporting observation of miscibility.

RESULTS AND DISCUSSION

Details concerning the description and application of the model to polymer mixtures has been presented previously on numerous occasions[1–6], and will not be duplicated in great detail here. In essence, the model allows for the calculation (equation (1)) of the interaction between two polymers, χ_{Blend}, as a function of the chemical composition of the components. For a mixture of polymers 1 and 2, composed of different mers or segments, χ_{Blend}, is an algebraic sum of the segmental exchange interactions, χ_{ij} which are weighted according to the relative abundance of the various segments. The

Table 1 Summary of composition of polymers

	Composition (segment volume fraction)[a]			
Polymer	ψ_A	ψ_B	ψ_C	ψ_D
PA-TMDT (Trogamid T)[b]	0.572	0.192	0.236	—
PA-6I (Nydur T40)	0.470	0.237	0.293	—
PA-6I/6T (Selar 3426)	0.470	0.237	0.293	—
Poly(ethylene terephthalate), PET	0.229	—	0.428	0.343
Poly(hexamethylene terephthalate), PHT	0.373	—	0.348	0.279

[a] Calculated using $\nu_A = 16.45 cm^3 mol^{-1}$, $\nu_B = 24.9 cm^3 mol^{-1}$, $\nu_C = 61.4 cm^3 mol^{-1}$, $\nu_D = 24.6 cm^3 mol^{-1}$: ref. 19

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

Table 2 Thermal properties and phase behaviour of blends of semi-aromatic polyamides with aliphatic co-polyesteramides

Molar composition of co-polysteramide LA/LO/LL (T_g°C)	ψ_B	ψ_D	PA-TMDT (T_g = 147°C) T_g (°C)	Phase behaviour	PA-6I (T_g = 118°C) T_g (°C)	Phase behaviour	PA6I/6T (T_g = 123°C) T_g (°C)	Phase behaviour
70.8/16.6/12.6 (18)	0.174	0.034	65	M	54	M	—	—
83.9/16.6 (23)	0.195	0.037	65	M	52	M	—	—
70.6/29.4 (4)	0.164	0.068			37	M	20,nd	PM
68.1/31.9 (6)	0.158	0.073			34	M	13,53	PM
61.9/38.1 (0)	0.144	0.088	60	M	—	—	—	—
60.6/39.4 (–9)	0.141	0.091			–5,90	I	–5,nd	I
56.8/43.2 (–13)	0.132	0.099			–15,nd	I	—	—
51.1/48.9 (–20)	0.119	0.112	37	M	–21,120	I	—	—
49.5/50.5 (–22)	0.115	0.116	38	M	—	—	—	
44.1/45.9 (–25)	0.103	0.129	–30,56	PM	—	—	—	—
43.4/46.0 (–30)	0.101	0.130	–30,102	I	—	—	—	—
40.0/60.6 (–35)	0.093	0.138	–35,120	I	–34,123	I	—	—
5.9/59.9/34.2 (16)	0.125	0.023	20,nd	I	16,nd	I	—	—

M = Miscible; PM = partially miscible; I = immiscible; nd = not determined segment volume fraction, ψ_i, is calculated from group contributions (ν_i) to the molar volume of polymers (see *Table 1*).

Homogeneous mixing, or miscibility, is characterized by the identity, $\chi_{\text{Blend}} < 0 < \chi_{\text{crit}}$, where χ_{crit} is determined, as usual[17], by the molecular mass of the polymers. For blends of polyamides and polyesters, χ_{crit} may be significantly greater than zero because of the relatively low molecular mass of these polymers when compared to addition polymers such as polystyrene.

$$\chi_{\text{Blend}} = \sum_{i,j} \psi_i^1 \psi_j^2 \chi_{ij} - \left[\sum_{i,j} \psi_i^1 \psi_j^1 \chi_{ij} + \sum_{i,j} \psi_i^2 \psi_j^2 \chi_{ij} \right] \tag{1}$$

Blends of aliphatic co-polyesteramides and aromatic polyamides

A summary of the blends investigated, and the associated thermal properties and phase behaviour, is presented in *Table 2*. It is already known that PA-TMDT and PA-6 form completely miscible blends; whereas, the polyester analogue of PA-6, polycaprolactone (PCL), forms completely immiscible mixtures with both PA-6[1] and PA-TMDT. Additionally, blends of the semi-aromatic polyamide PA-MXD6 with LA/LO copolymers have been shown[3] to have a more unfavourable interaction as the lactone content of the co-polyesteramide increases. Therefore, we should expect to find an analogous situation in the equivalent blends based on PA-6I, PA-6I/6T and PA-TMDT.

It is evident from *Table 2* that this is indeed the case and that blends can tolerate a relatively large quantity of the lactone in the co-polyesteramide before phase separated mixtures are produced. For PA-TMDT this occurs at approximately 46 mol% lactone. For blends based upon PA-6I a lactone content of approximately 35% is required to effect the same behaviour. A similar observation is noted for PA-6I/6T confirming once again that partial replacement of the 1,3- by 1,4-isomer has a negligible effect on phase behaviour.

Some thermograms are reproduced as *Figure 1* in order to illustrate the clarity of phase behaviour that was usually encountered. Note that a small level of crystallization of the copolymer has occurred in the blend with PA-6I, probably the result of the slightly lower T_g in the blend when compared to the blend with PA-TMDT. Although not shown, it is also possible to detect a broadening of the T_g of the blends as the critical lactone content of the copolymer is approached. Such behaviour, taken in conjunction with the observations noted above concerning the large lactone content required to induce immiscibility, supports the view that miscibility in aliphatic/semi-aromatic blends is driven by a favourable interaction, i.e. χ_{Blend} is negative.

The fact that the PA-6I blends require less caprolactone in the copolymer to produce immiscibility, when compared to blends based on PA-TMDT, represents an important observation when considering the nature of the interactions responsible for miscibility in binary polyamide blends. Calculations have shown that the blend of PA-6I with PA-6 has a far greater favourable interaction ($\chi_{\text{Blend}} \approx -0.022$) for miscibility than that estimated for PA-TMDT/PA-6 ($\chi_{\text{Blend}} \approx -0.005$)[16,17].

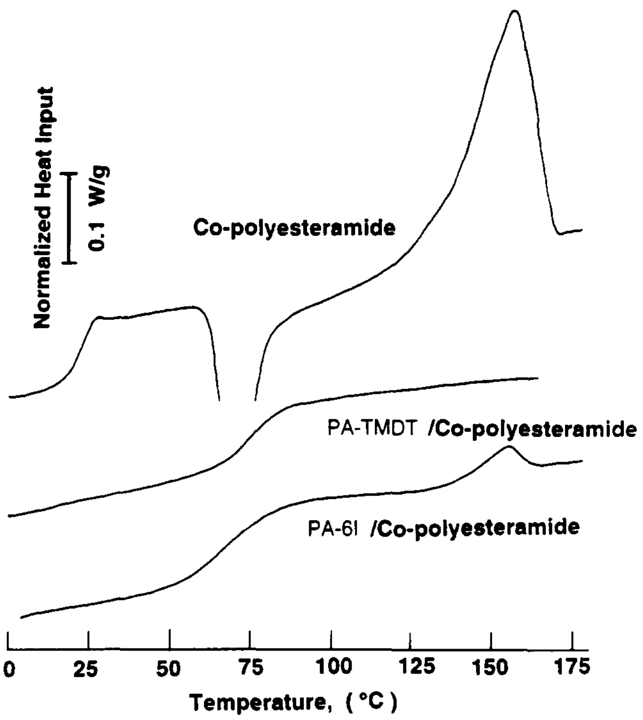

Figure 1 D.s.c. thermograms of the co-polyesteramide (LA:LO:LL; 70.8:16.6:12.6) and its miscible blends with PA-6I and PA-TMDT, respectively

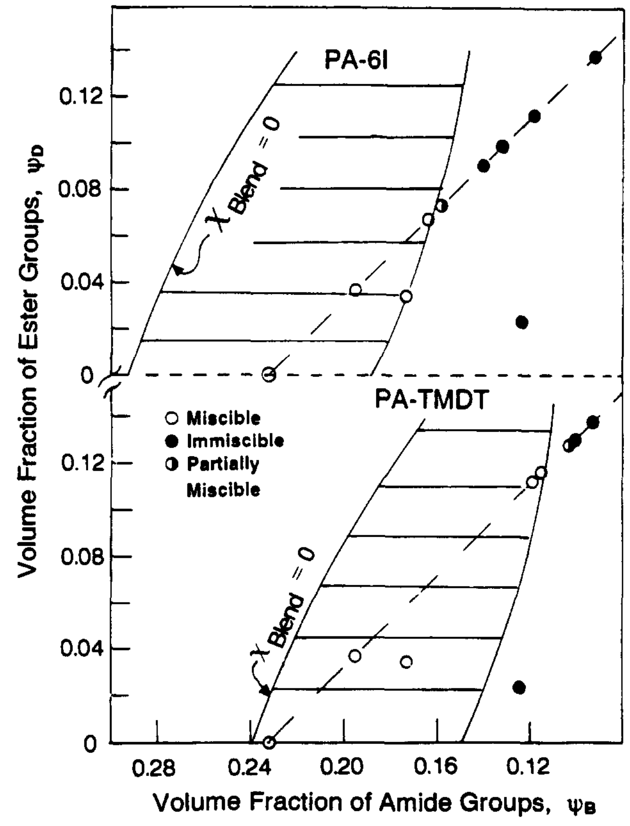

Figure 2 Comparison of experimental phase behaviour and model calculations of blends of aromatic polyamides PA-6I and PA-TMDT, respectively, with co-polyesteramides (*Table 2*). Shaded area is where $\chi_{\text{Blend}} < 0$. Calculations obtained using: $\chi_{\text{AB}} = 8.53(4)$, $\chi_{\text{AC}} = -0.30(8)$, $\chi_{\text{AD}} = 2.23(3)$, $\chi_{\text{BC}} = 7.97(4)$, $\chi_{\text{BD}} = 3.88(0)$, $\chi_{\text{CD}} = 1.69(2)$

However, it may be argued that on the basis of the relative amounts of amide groups in the two semi-aromatic polyamides (see *Table 1*), the PA-6I blend should require the greater lactone content in the co-polyesteramide to induce immiscibility. Although the experimental observation may be regarded as contrary to expectations, it will be shown, as detailed below, that this result is perfectly consistent with predictions derived from the model applied here.

For blends of aromatic polyamides, defined as ABC polymers, and co-polyesteramides (ABD polymers) all the segmental interaction parameters, χ_{ij}, necessary for calculating χ_{Blend} are available from information published previously. Accordingly, using $\chi_{\mathrm{AB}} = 8.53(4)$[1] to scale segmental interaction parameters derived from miscible binary polyamide blends[16,17] results in $\chi_{\mathrm{AC}} = -0.30(8)$ and $\chi_{\mathrm{BC}} = 7.94(7)$. Values of $\chi_{\mathrm{AD}} = 2.23(3)$ and $\chi_{\mathrm{BD}} = 3.88(0)$ were obtained from analysis of aliphatic polyamide/polyester blends[1]. The remaining parameter, the phenyl-ester interaction, χ_{CD}, required for calculating the phase behaviour, is available as an estimation ($\chi_{\mathrm{CD}} = 1.5$[3]); however, a more desirable approach would involve using the data presented in *Table 2* to derive a more reliable determination of this quantity. There are some problems associated with this procedure; most notably the fact that configuration of species would have to be neglected as an influence on χ_{ij}. In particular, the value that would be obtained for χ_{CD} represents the interaction of an aliphatic ester group with a phenyl group in a BCB configuration[3]. It is worth noting that the data presented in *Figure 2* can be described fairly adequately using the χ_{ij} noted above which have been obtained independently of any of the data shown here.

If no distinction is made between 1,4- and 1,3-phenyl isomers and defining $\chi_{\mathrm{Blend}} = 0$ for PA-TMDT in a co-polyesteramide containing 49% caprolactam, a value of $\chi_{\mathrm{CD}} = 1.69(2)$ is obtained. It is also noteworthy to find that the value obtained is very close to that noted above. A pictorial representation of the result is shown as part of *Figure 2* for blends of PA-TMDT in co-polyesteramides. The shaded region indicates $\chi_{\mathrm{Blend}} < 0$. The fit of the data to the model is also capable of providing good agreement with the two co-polyesteramides that contain laurolactam.

Once again, neglecting the effects of isomerism of the phenyl group also allows the use of these same parameters to calculate the behaviour of PA-6I and PA-6I/6T in co-polyesteramides and to compare the results with those obtained experimentally as shown in *Table 2*. Also shown as part of *Figure 2*, it should be noted that the agreement is quite good.

Blends of aliphatic polyamides and semi-aromatic polyesters

If semi-aromatic polyesters are again defined using the most simple nomenclature (ACD), and disregarding any affects which arise from the configuration of segments and isomerism, then the information above may be used to perform some exploratory calculations on blends of aliphatic polyamides with polyesters such as PET. For these calculations a value of $\chi_{\mathrm{AC}} = 0.1$[3] has been used rather than the value used to obtain the information in *Figure 2*. This represents a minor discrepancy but it is probably a more appropriate choice based on the earlier studies[3]. Calculations describing the behaviour of some representative polyamide–polyester blends are shown in *Figure 3*. The interaction in blends based on PBT will be intermediate between those shown for PHT and PET and will therefore not differ significantly.

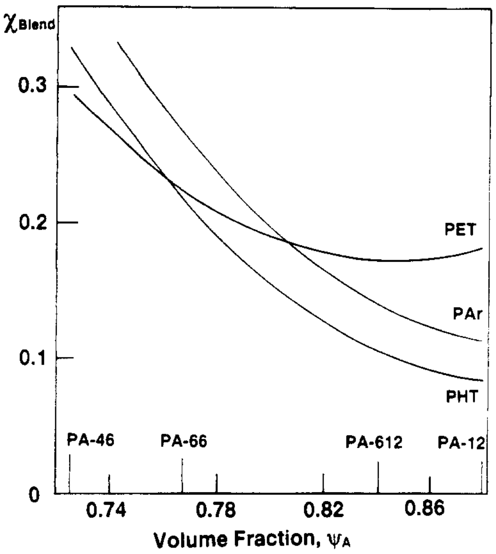

Figure 3 Calculated values of χ_{Blend} for blends of aliphatic polyamides and semi-aromatic polyesters, as a function of methylene content ψ_{A} of polyamide. Obtained using $\chi_{\mathrm{AB}} = 8.53(4)$, $\chi_{\mathrm{AC}} = 0.1$, $\chi_{\mathrm{AD}} = 2.23(3)$, $\chi_{\mathrm{BC}} = 7.97(4)$, $\chi_{\mathrm{BD}} = 3.88(0)$, $\chi_{\mathrm{CD}} = 1.69(2)$

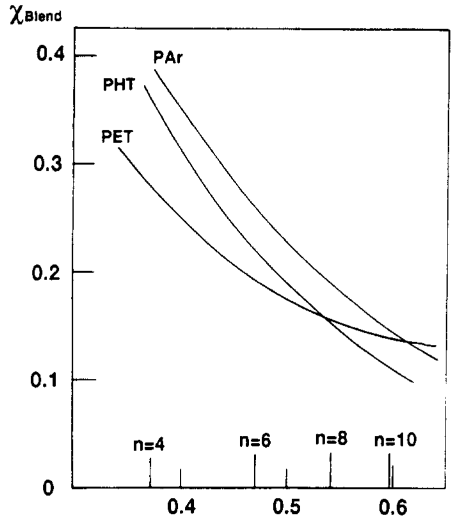

Figure 4 Calculated values of χ_{Blend} for blends of aromatic polyamides -(CH$_2$)$_n$ NHCO phenyl CONH- and semi-aromatic polyesters, as a function of methylene content (ψ_{A}) of polyamide. Obtained using $\chi_{\mathrm{AB}} = 8.53(4)$, $\chi_{\mathrm{AC}} = 0.1$, $\chi_{\mathrm{AD}} = 2.23(3)$, $\chi_{\mathrm{BC}} = 7.97(4)$, $\chi_{\mathrm{BD}} = 3.88(0)$, $\chi_{\mathrm{CD}} = 1.69(2)$

Included in the calculation is a tentative estimation for polyarylate, PAr, which is typically a copolymer of bisphenol A and a mixture of isophthalic and terephthalic acids. Representing PAr as a polymer of A, C, and D segments whose respective χ_{ij} are identical to those presented above is a large over simplification; however, if segmental interaction parameters are only slightly influenced by configuration the general trend shown will not be significantly influenced. For all the polyesters noted in *Figure 3* there is a shift in the curves to lower values of χ_{Blend} as the methylene content of the aliphatic polyamide increases; nevertheless, the general trend is that a highly unfavourable interaction exists between these polymers; a result which is generally supported by experimental data.

Blends of semi-aromatic polyamides and semi-aromatic polyesters

The same set of segmental interaction parameters can be applied to provide an estimation of the interaction in blends of semi-aromatic polyamides and semi-aromatic polyesters. Presented as *Figure 4*, the results are essentially the same as those noted above for the aliphatic polyamides, indicating a rather unfavourable interaction for miscibility. There is only a little experimental evidence to corroborate the predicted trends; however, studies[9,20] of a number of blends of different semi-aromatic polyamides, including PA-TMDT, indicate immiscibility should be expected. Interestingly, the latter study[20] also suggested that miscible blends could be obtained with semi-aromatic polyamides and PAr, under certain conditions, by substitution of some of the iso/terephthalic acid in the PAr with a t-butyl-substituted diacid. Notwithstanding the simplifications introduced in order to conduct the analysis presented above, it is not clear why this should occur. The introduction of t-butyl substituted segments would be expected to have only a slight influence on the χ_{ij} and their resulting effect would not be expected to overcome the extremely unfavourable interaction indicated in the calculations presented here. Evidently, the information presented in *Figures 3* and *4* should be viewed only as tentative, especially with regard to the projected behaviour of PAr, until more detailed information is available for consideration.

CONCLUSIONS

Miscibility in blends of semi-aromatic polyamides, derived from aliphatic diamines and benzene–dicarboxylic acids, containing aliphatic co-polyesteramides obeys simple relationships that appear to depend primarily upon the chemical composition of the constituents. Formalizing the observed behaviour in terms of a binary interaction model emphasizes the utility of copolymers in establishing, semi-quantitatively, structure–interaction relationships in blends that exhibit exclusively unfavourable interactions. The segmental interaction parameters derived here may be obtained by alternative strategies using copolymers based upon semi-aromatic co-polyesteramides. Synthetic routes to these copolymers, are readily available[21] and future investigations of blends based on these materials may help to clarify some of the issues discussed above concerning configuration of segments and their influence on segmental interaction parameters.

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