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Miscibility and crystallization of semicrystalline nylon 6 and amorphous nylon 6IcoT blends

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Injection-moulded semicrystalline nylon 6 and amorphous nylon 6IcoT blends were homogeneous (single glass transition, T_g) but metastable. Annealing above T_g increased crystallinity and induced phase separation probably due to crystallization and differences in polymer stiffness and spatial geometry. Crystallization of the nylon 6 component was greater than that of the pure nylon 6 in some blends since dilution with nylon 6IcoT would have decreased the number of tie molecules and increased the mobility of nylon 6 molecules. Microcrystals formed during annealing and their melting temperature and melting energy depended on composition. There was no evidence for significant transamidization between nylon 6 and nylon 6IcoT during injection moulding and annealing.

(Keywords: nylon 6/nylon 6IcoT blends; miscibility; crystallization)

INTRODUCTION

Blending polymers creates materials whose properties depend on the composition, microstructure and processing. Therefore, to control their properties, understanding their miscibility becomes paramount because it determines the microstructure and phase morphology. The relation of microstructure and mechanical properties of miscible and immiscible polymer blends has been described[1–4] and understanding this relationship has been an active area of research.

The Gibbs free energy of mixing, ΔG_m, is the basis for understanding miscibility of polymer blends

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (1)$$

where ΔH_m is the heat of mixing and ΔS_m is the entropy of mixing. The heat of mixing due to dispersive forces can be expressed in terms of the solubility parameter of the pure components

$$\Delta H_m = V(\delta_1 - \delta_2)^2\phi_1\phi_2 \qquad (2)$$

where δ_1 is the solubility parameter of component i and ϕ_i is the volume fraction. Equation (2) indicates that van der Waals type interaction always results in a positive heat of mixing.

The entropy of mixing ΔS_m for polymer blends is given in Flory[5] as

$$\Delta S_m = -R\left[\frac{\phi_1}{V_1}\ln\phi_1 + \frac{\phi_2}{V_2}\ln\phi_2\right] \qquad (3)$$

where R is the gas constant and V_i is the molar volume. ΔS_m is negligibly small since V_i is usually large for polymers. Therefore, equations (1)–(3) always predict immiscible polymer blends. However, if ΔH_m is negative due to specific interactions between the blend components such as hydrogen bonds[6], acid–base attraction[7], ion–ion interaction[8], and n–π complex formation[9], miscibility will be possible. An excess energy term $\chi\phi_1\phi_2$ has been added to equation (1) to account for the specific interactions and the interaction parameter χ is negative if there is exothermic mixing due to any of the above-mentioned interactions. Other factors such as crystallization, differences in polymer stiffness and spatial geometry can also affect the free energy of mixing and are included in χ[10–15].

For polymer blends with at least one semicrystalline component, 'miscibility' refers only to the amorphous phase. The crystallization kinetics, the degree of crystallinity and crystal size distribution are functions of the blend thermal history. Work by several researchers has shown that the higher T_g component at low concentrations can act as crystallization nuclei and increase the degree of crystallinity; however, at higher concentrations molecular mobility is reduced and the crystallinity decreases[16–18]. Blending with a lower T_g polymer acts as a diluent, which increases chain mobility and consequently the degree of crystallinity increases[19]. However, it has also been reported that blending a semicrystalline polymer with an amorphous one does not affect the degree of crystallinity[20].

For semicrystalline/amorphous polymer blends, X-ray diffraction studies indicate that the crystal structure of the blends is the same as the unblended polymer, but the degree of crystallinity and the crystal perfection may change with blend composition[21]. The melting point depends on the interaction parameter χ; for a negative χ

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melting point depression is observed, which can be used to detect miscibility[22]. Since the melting point is also influenced by the crystal size and perfection, corrections need to be made when using the melting point depression to calculate the interaction parameter χ[23].

Recently, there has been interest in aromatic amorphous polyamides and their blends with amorphous and semicrystalline polymers, especially with semicrystalline nylons[20,24]. Aromatic polyamides are attractive thermoplastic materials for use in certain chemical environments due to their resistance to oxygen transport and other chemicals; they also have good dimensional stability and dielectric properties. These properties are attributed to their chemical structure, which is shown in *Figure 1*. An aliphatic section of nylon is replaced by an aromatic ring which reduces chain mobility, and increases tensile properties and T_g (130–180°C) relative to the aliphatic nylons[25], and they tend not to crystallize. This paper describes the miscibility, crystallization and phase behaviour of nylon 6/nylon 6IcoT blends as a function of composition and annealing characterized by differential scanning calorimetry (d.s.c.).

EXPERIMENTAL

Materials

The blends were fabricated from nylon 6, an Allied-Signal material and nylon 6IcoT, a Du Pont product. Nylon 6 is semicrystalline and its crystallinity depends on processing, subsequent annealing and moisture content. The T_g of this nylon 6 was 47°C and the T_m was 223°C. Nylon 6IcoT is a condensation product of 1,6-hexanediamine and a mixture of isophthalic acids (iso/terephthalic acid, hexamethylene diamine)[20]. The T_g of nylon 6IcoT was 127°C. The nylon 6/nylon 6IcoT blends of 0/100, 20/80, 40/60, 60/40, 80/20, and 100/0 by weight were supplied by Allied-Signal Inc. Pellet mixtures were dry blended and extruded on a Killion 100, 25.4 mm extruder at 260°C. The blends were then injection moulded into ASTM type II tensile bars and 6.35 x 12.7 x 125 mm bend bars. Some of the samples were vacuum annealed before testing.

Thermal analysis

Differential scanning calorimetry (d.s.c.), with a Du Pont 2000 Thermal Analyzer, determined the onset glass transition temperature T_g, the crystallization temperature T_c, and the melting temperature T_m. T_c and T_m were taken as the maximum and minimum in the exothermic and endothermic peaks, respectively. The degree of crystallinity was calculated from the area of the melting endotherm divided by the reported heat of fusion for nylon 6 crystals ($\Delta H_f = 230\ \mathrm{J\ g^{-1}}$)[26]. D.s.c. samples weighed 5–10 mg, and the scanning rate was 20°C min^{-1}.

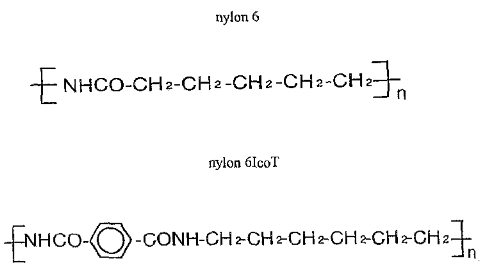

Figure 1 Chemical structures of nylon 6 and nylon 6IcoT

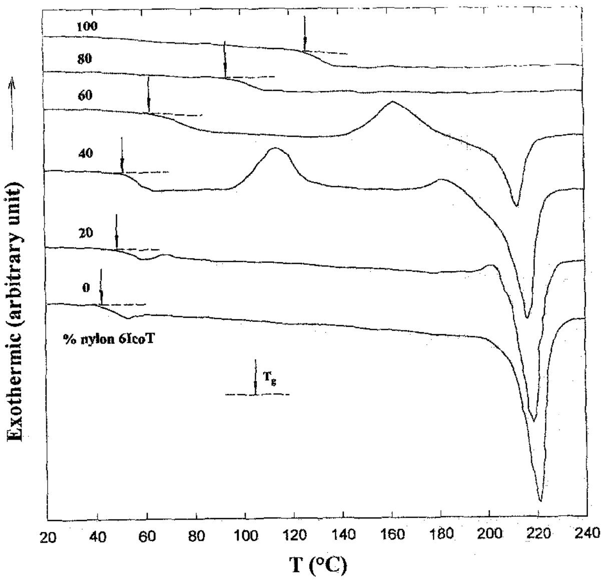

Figure 2 D.s.c. thermograms of the as-moulded nylon blends

RESULTS

Thermal properties

Figure 2 shows the d.s.c. thermograms for the as-moulded nylon blends. The pure nylon 6 and the 20% nylon 6IcoT blend have one T_g and one melting endotherm. However, the 40 and 60% nylon 6IcoT blends show a crystallization exotherm between T_g and T_m. The area of the melting endotherm depends on the concentration of nylon 6 and is greater than the area of the exotherm, indicating that crystals were present in the as-moulded samples, and additional crystallization occurred during heating. The 80% nylon 6IcoT blend and pure nylon 6IcoT had a single T_g with no evidence of crystallization or melting during heating.

Figure 3 shows the d.s.c. thermograms of the blends after annealing at 100°C for 24 h. They differ from the thermograms of the as-moulded blends (*Figure 2*) in two ways: (1) there is a small endotherm peak at about 120°C

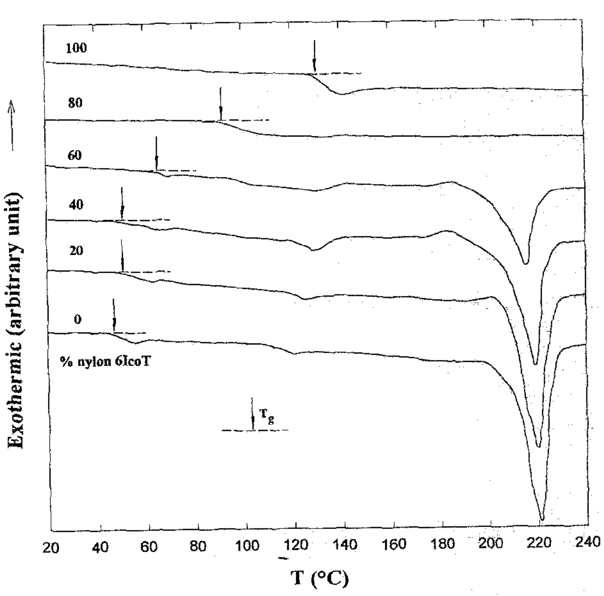

Figure 3 D.s.c. thermograms of the nylon blends annealed at 100°C for 24 h

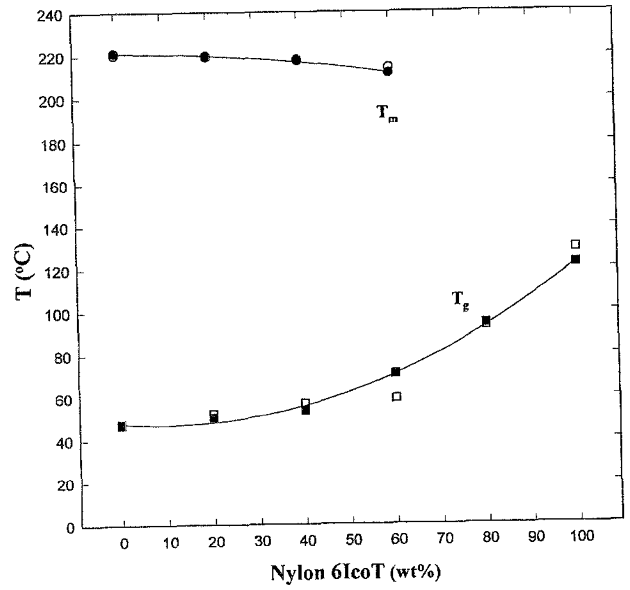

Figure 4 T_g and T_m of the nylon blends (filled symbols are for the as-moulded blends and open symbols are for the blends annealed at 100°C for 24 h)

for blends with nylon 6IcoT content less than or equal to 60%, and (2) crystallinity was close to the equilibrium amount after annealing since there were no exotherms during the d.s.c. test. Pure nylon 6IcoT and the 80% nylon 6IcoT blend had no detectable crystals.

The T_g of the blends increased with increasing nylon 6IcoT content, but T_m decreased as shown in *Figure 4*.

Crystallization

The crystallinity of the nylon blends was calculated according to

$$X_{\text{blend}} = \frac{\Delta H}{\Delta H_n} \times 100 \tag{4}$$

where X_{blend} is the percentage crystallinity, ΔH (J g^{-1}) is the heat of fusion of the blend, and ΔH_n is the heat of fusion for 100% crystalline nylon 6 (230 J g^{-1})^{26}.

On the d.s.c. trace of the as-moulded 40% blend (*Figure 2*), there is an exothermic peak just before the melting peak, indicating further crystallization before melting. Continuous crystallization between the two exotherms is also probable. To demonstrate that the exothermic peak during d.s.c. heating was due to crystallization, the 40 and 60% blends were heated in the d.s.c. above their melting temperatures and then quenched in liquid nitrogen. Second scans immediately after quenching at 20°C min^{-1} are shown in *Figure 5*. A base line connecting points A and B was drawn which represents the hypothetical d.s.c. curve if neither crystallization nor melting occurred during the d.s.c. test. The area above this base line (area I) is the exothermic energy of crystallization and the area below (area II) is the endothermic melting energy. The area of the crystallization exotherm (area I) equalled the area of the melting endotherm (area II) within experimental error for both blends. This means that the area of the exotherm should be subtracted from the endotherm as shown in *Figure 5* to determine the crystallinity in the as-moulded samples for the 40 and 60% nylon 6IcoT blends. This was not necessary for the other blends because further crystallization did not occur during the d.s.c. tests.

The crystallinity of the nylon 6 component in the

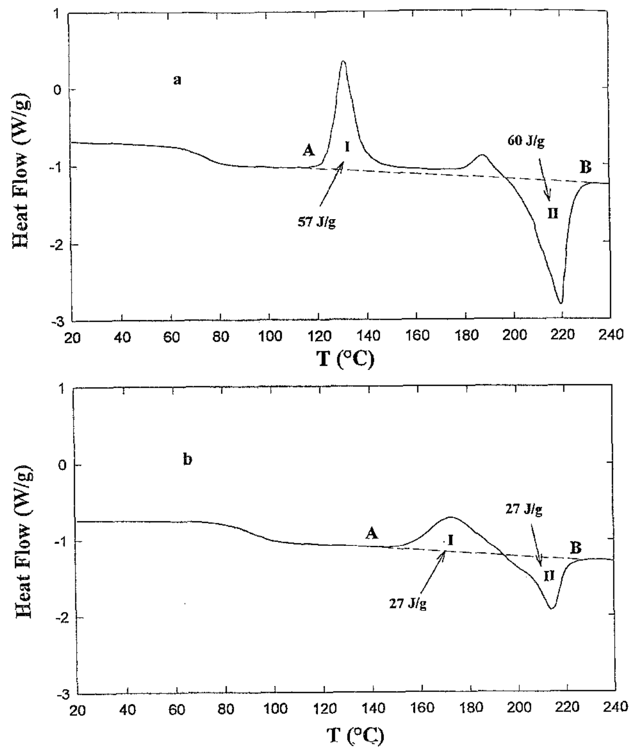

Figure 5 D.s.c. thermograms of the 40% (a) and 60% blends (b) after melt quenching

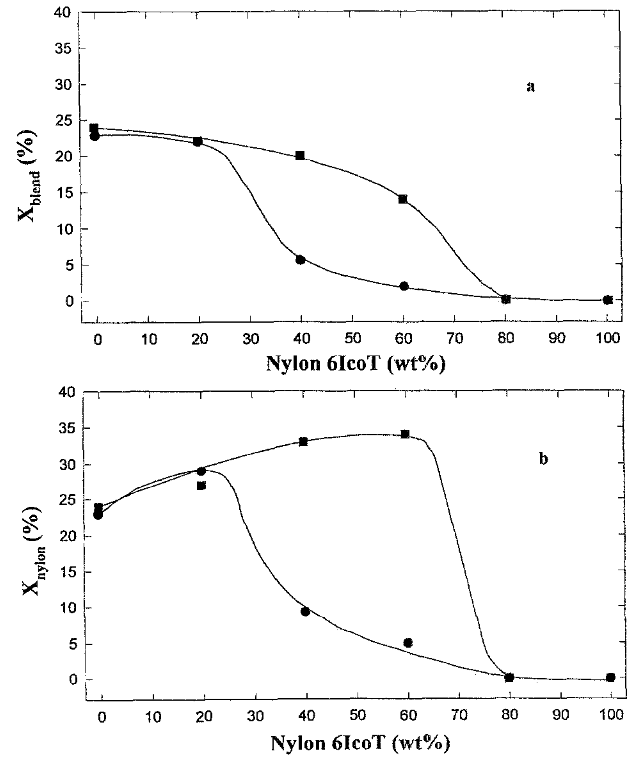

Figure 6 Degree of crystallinity of the nylon blends, X_{blend} (a) and of nylon 6, X_{nylon} (b); (●): as-moulded; (■): annealed at 100°C for 24 h

blends was calculated according to

$$X_{\text{nylon}} = \frac{\Delta H}{\Delta H_f \phi_n} \times 100 \tag{5}$$

where ϕ_n is the weight fraction of nylon 6. X_{blend} and X_{nylon} are shown as a function of composition in *Figure 6*. X_{blend} of both as-moulded and annealed blends decreased as the nylon 6IcoT content increased, and only X_{blend} for the 40 and 60% blends increased after annealing. However, X_{nylon} for annealed blends increased with nylon 6IcoT concentration except for the completely amorphous 80 and 100% nylon 6IcoT blends. In the as-moulded blends, only X_{nylon} for the 20% blend was higher than the pure nylon 6, and X_{nylon} for the rest of the blends decreased with nylon 6IcoT content.

Values of T_g, T_m and the degree of crystallinity are summarized in *Table 1* for the as-moulded blends and in *Table 2* for the annealed blends.

In addition to annealing at 100°C for 24 h, some specimens were annealed for longer times and/or at higher temperatures. Annealing always caused a small endotherm on the d.s.c. traces about 20°C higher than the annealing temperatures (*Figures 3* and *7*). The minimum temperature in the endotherm, $T_{\mu m}$, and the area of the endotherm, ΔH, are listed in *Table 3* and plotted in *Figures 8* and *9*, respectively.

DISCUSSION

T_g *and* T_m

Miscible blends form a single amorphous phase, and as a result they have a single, composition-dependent T_g that might follow the Fox equation[27]

$$\frac{1}{T_g} = \frac{\phi_1}{T_{g1}} + \frac{\phi_2}{T_{g2}} \tag{6}$$

or the Gordon–Taylor equation[28]

$$T_g = \frac{\phi_1 T_{g1} + k\phi_2 T_{g2}}{\phi_1 + k\phi_2} \tag{7}$$

Table 1 T_g, T_m, X_{blend} and X_{nylon} of as-moulded nylon blends

Nylon 6IcoT (wt%)	T_g (°C)	T_m (°C)	X_{blend} (wt%)	X_{nylon} (wt%)
0	46.8	221.1	23.0	23.0
20	50.4	219.3	22.0	29.0
40	53.4	217.3	5.6	9.3
60	70.7	211.5	2.0	5.0
80	94.1	–	0	0
100	122.0	–	0	0

Table 2 T_g, T_m, X_{blend} and X_{nylon} of nylon blends annealed at 100°C for 24 h

Nylon 6IcoT (wt%)	T_g (°C)	T_m (°C)	X_{blend} (wt%)	X_{nylon} (wt%)
0	47.3	220.2	24.0	24.0
20	52.1	219.8	22.0	27.0
40	57.0	218.0	20.0	33.0
60	59.0	214.0	14.0	34.0
80	93.0	–	0	0
100	129.0	–	0	0

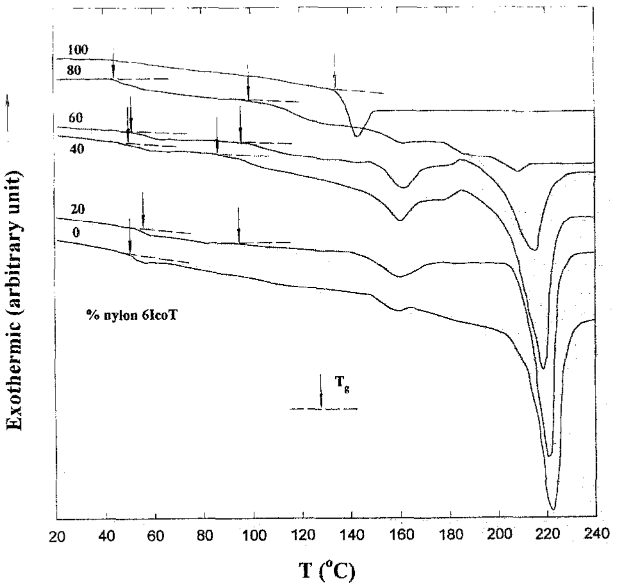

Figure 7 D.s.c. thermograms of the nylon blends annealed at 100°C for 5 days + 140°C for 2 days + 120°C for 3 days

Table 3 $T_{\mu m}$ and melting energy of annealing-induced microcrystals: (I) 100°C for 1 day; (II) 100°C for 5 days; (III) 100°C for 5 days + 140°C for 2 days + 120°C for 3 days

	I		II		III	
Nylon 6IcoT (wt%)	$T_{\mu m}$ (°C)	ΔH (J g^{-1})	$T_{\mu m}$ (°C)	ΔH (J g^{-1})	$T_{\mu m}$ (°C)	ΔH (J g^{-1})
0	112.8	1.0	125.8	2.0	153.8	1.9
20	116.5	1.7	128.6	2.6	159.5	5.2
40	123.1	3.0	131.2	4.5	158.5	5.9
60	123.0	1.7	131.5	3.4	160.3	5.7
80	–	–	–	–	161.2	2.5
100	–	–	–	–	142.5	3.0

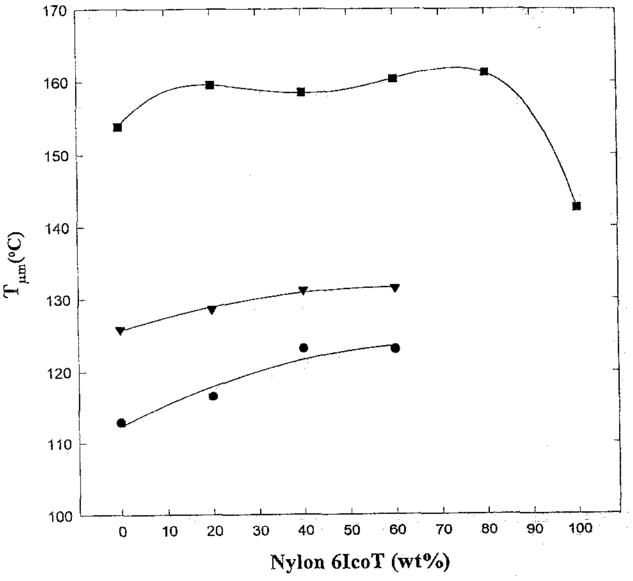

Figure 8 $T_{\mu m}$ of annealing-induced microcrystals: (●) 100°C for 1 day; (▼) 100°C for 5 days; (■) 100°C for 5 days + 140°C for 2 days + 120°C for 3 days

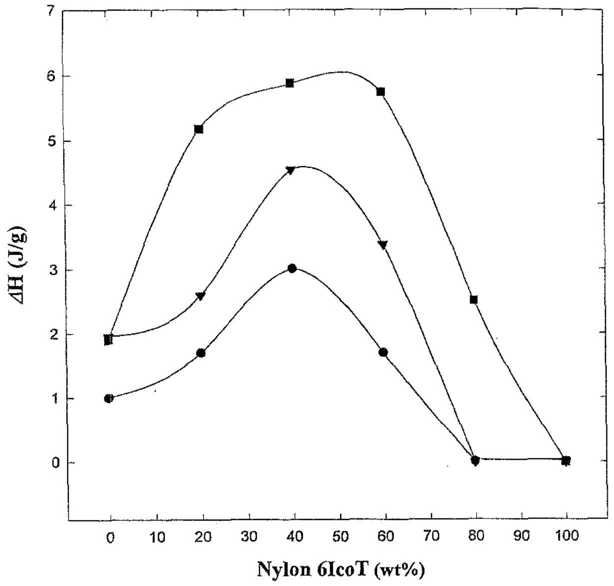

Figure 9 Melting energy ΔH of annealing-induced microcrystals: (●) 100°C for 1 day; (▼) 100°C for 5 days; (■) 100°C for 5 days + 140°C for 2 days + 120°C for 3 days

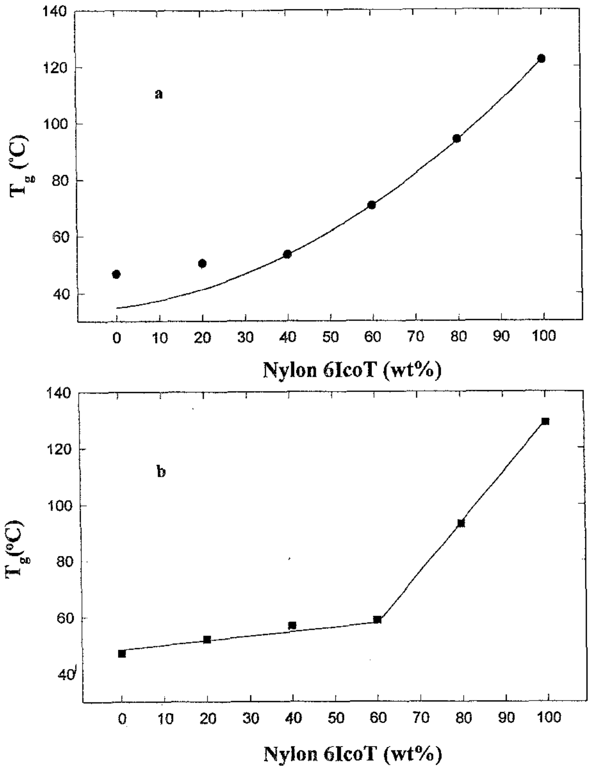

Figure 10 T_g of the nylon blends (a) as-moulded (solid line represents the Gordon–Taylor equation); (b) annealed

where ϕ_i is the volume fraction of the components and k is an adjustable parameter. However, the T_g data for the as-moulded and the annealed blends fit neither the Fox nor the Gordon–Taylor equation if 47°C was taken as T_{g1} (nylon 6) and 122°C as T_{g2} (as-moulded nylon 6IcoT) or 129°C as T_{g2} (annealed nylon 6IcoT). Calculating the weight fraction of amorphous nylon 6 and nylon 6IcoT by neglecting the nylon 6 crystals did not improve agreement with either equation. It should be noted that the T_g of semicrystalline nylon depends on the crystallinity; for example, a change in crystallinity from 5 to 50% could increase T_g by 13°C[29]. Therefore, 47°C may not be the appropriate T_g for nylon 6 considering that the Fox and the Gordon–Taylor equations were originally developed for polymer solutions and copolymers without crystals. A T_g for pure glassy nylon 6 is difficult to obtain because the crystallization of nylon 6 is rapid. The Gordon–Taylor equation was then used to fit the T_g data of the glassy as-moulded blends (blends with 40, 60, 80 and 100% nylon 6IcoT). With the adjustable coefficient $k = 0.45$, the extrapolated T_g for nylon 6 was 35°C. In *Figure 10a*, the T_g values for the glassy blends fit the Gordon–Taylor equation well, but the T_g for blends with crystals lie above the theoretical curve. This is consistent with crystals lowering the mobility of molecules and increasing the T_g[30].

The T_gs of the annealed blends increased linearly with increasing nylon 6IcoT content up to 60% (*Figure 10b*), indicating partial miscibility and representing the phase rich in nylon 6. The T_gs for the nylon 6IcoT-rich phases were not detectable, possibly because they overlapped the small endothermic peaks between T_g and T_m (*Figure 3*). There is only one T_g for the 80% blend in *Figure 3* because the amount of nylon 6-rich phase is too small to allow detection of its T_g. Therefore, the T_g data for the annealed blends cannot be fitted with a single smooth curve.

Crystallization

Blending nylon 6 with nylon 6IcoT depressed the melting point and increased T_g (*Figure 4*). This reduces the crystallization gap ($T_m - T_g$) and would decrease the crystallinity because of reduced nucleation and molecular mobility.

Figure 6a shows that dilution of nylon 6 with nylon 6IcoT decreased the crystallinity of the blends, and annealing at 100°C for 24 h only increased the crystallinity of the 40 and 60% blends. Some conclusions from these results are that (1) crystallization in the pure nylon 6 and 20% nylon 6IcoT blend was rapid and injection moulding (a quench) did not affect this process; (2) pure nylon 6IcoT and the 80% nylon 6IcoT blend have no or little tendency to crystallize (there may have been some nylon 6 crystals in the 80% blend but they were below the level of detectability); (3) injection moulding retarded the crystallization of the 40 and 60% blends because there was insufficient time for the molecules to crystallize. Therefore, annealing increased their crystallinity simply by providing sufficient thermal energy to increase molecular mobility and sufficient time for molecular movement.

Figure 6b shows that blending increases the nylon 6 crystallinity (X_{nylon}) in the 20% as-moulded blend and in the 20, 40 and 60% annealed blends so that it is greater than that of pure nylon 6. Since entanglements and tie molecules limit the extent of crystallinity, then in a blend with fewer crystals, but with sufficient mobility and time, the crystallinity of the crystallizable component could be greater than in pure nylon 6 samples because fewer of the nylon 6 molecules would be tie molecules.

A suggested alternative explanation for semicrystalline/amorphous nylon blends[18] is that the more rigid amorphous molecules act as nucleation sites, but this does not apply in this system. If the amorphous molecules acted as nuclei then the crystallization temperature should increase with increasing nylon 6IcoT, but cooling d.s.c. experiments showed that the crystallization temperature was depressed by increasing nylon 6IcoT, which could be due to fewer nuclei and/or lower mobility.

In *Figure 3*, there is a small endothermic peak at about 120°C on the d.s.c. traces of the blends after annealing at 100°C for 24 h. It has been reported that microcrystals form in the amorphous phase of nylon 6 during annealing and their melting temperature (120–230°C) depends on the annealing temperature and time[31]. These so-called microcrystals were also found in other semicrystalline polymers and it is common for the T_ms of these microcrystals to be 10–30°C higher than the annealing temperature[32]. If the small endotherm of the annealed nylon blends with nylon 6IcoT content up to 60% is due to the melting of microcrystals (*Figure 3*), their melting temperatures should be a function of the annealing temperature. It is shown in *Figure 7* that, for the blends annealed at 140°C, the small endotherms shifted to higher temperatures and they are still about 20°C higher than the annealing temperature. Therefore, besides the nucleation and growth of normal crystals during annealing, some microcrystals were formed.

Figure 8 shows that the melting temperature of the microcrystals increases with increasing nylon 6IcoT content. If the microcrystals are nylon 6, their T_m should decrease with increasing nylon 6IcoT because of the melting point depression phenomenon, as well as the expectation that the nylon 6 microcrystals would be smaller in the blends with higher nylon 6IcoT content. Therefore, the structure and perfection of these so-called microcrystals must differ from that of the primary nylon 6 crystals and they may vary with composition[20,33]. The melting energy of microcrystals as a function of composition, shown in *Figure 9*, has a maximum at about 50% nylon 6IcoT. It is likely that the heat of fusion of the microcrystals depends on the structure and perfection, and hence on composition. Therefore, the amount of microcrystals cannot be calculated. Their melting temperature $T_{\mu m}$ and exothermic energy ΔH are listed in *Table 3*.

Phase behaviour

Based on the melting point depression (shown in *Figure 4*) the calculated Flory–Huggins interaction parameter χ_0 is negative, which implies that the nylon 6 and nylon 6IcoT could be miscible, and therefore well mixed above the melting temperature. This homogeneity was frozen in during injection moulding, as shown by the composition-dependent T_g (*Figure 2*). However, *Figure 7* shows two T_gs on the d.s.c. trace of each blend, indicating that annealing at 140°C induced crystallization and phase separation. In fact, phase separation probably occurred during annealing at 100°C (*Figure 3*), but the T_g for the nylon 6IcoT-rich phase was not discernible because the melting of the microcrystals was superimposed by T_gs of nylon 6IcoT-rich phases[34]. Annealing-induced crystallization and phase separation (two T_gs) was also noticed by Ellis in other, but similar nylon blends[20,35,36].

The mean-field binary interaction model, developed by Ellis to predict the phase behaviour of nylon blends, predicts the nylon 6/nylon 6IcoT blend to be miscible, in agreement with our results for the injection-moulded samples. Ellis has not published any results on the phase behaviour of annealed nylon 6/nylon 6IcoT blend, but he studied a similar semicrystalline/amorphous nylon blend, nylon 6/nylon 3Me6T which, according to his theory, should be miscible over the entire range of composition; however, annealing caused crystallization and phase separation which was entropic[20,35], morphological[37], or both in origin. These results are analogous to those presented in this paper. Another semicrystalline/amorphous nylon blend, nylon 11/nylon 12IA, was completely miscible when prepared in the amorphous state, but became partially miscible after crystallization[35]. Both miscible and immiscible phase behaviour was found in amorphous nylon 3Me6T/nylon 6IcoTA blends. These examples of phase behaviour contrary to theory have been attributed to the history of the polymers, that is their origin, thermal history, and residual content, etc.[36].

On a more fundamental level the primary cause of phase separation in this system may be attributed to entropic effects which were not taken into account in Ellis' theory. Two theories of entropic effects relevant to our system are: (1) crystallization expels the amorphous nylon, even though the two components were completely miscible in the melt, and leads to phase separation[38–41] and (2) differences in the statistical segment length (similar to the repeat unit length)[10], which is dependent on the stiffness of the polymer[12], and the differences in the spatial geometry can lead to phase separation. Quantitative evaluation of the contribution of crystallization and other entropic effects to the phase separation in this system has not been done, but qualitatively they help rationalize the observed phase behaviour in these nylon blends.

Transamidization can affect the phase behaviour of polyamide blends. To determine if transamidization occurred, the molecular weight distribution of the pure components and the 20% blend after injection moulding and annealing were measured. The blend with 20% nylon 6IcoT had 'a bimodal molecular weight distribution similar to the sum of the two individual components. Both types of nylon underwent some degradation, but there was little evidence of interchange between the species'[42]. In addition, blends annealed for 90 min at 260°C plus 24 h at 140°C still had two T_gs, which supports the conclusion based on the molecular weight study. Further evidence that significant transamidization did not occur is that the crystallinity of the nylon 6 component in the blends increased (*Figure 6b*), but if transamidization had occurred it would have decreased[20,43], especially in the middle range of composition where the reaction would be most pronounced. Again, the extensive studies on nylon 3Me6T/nylon 6 blends by Ellis[20] showed that the low-level thermal exposure during blend preparation (moulding and drying) was not sufficient to cause such transreaction. Thus, transamidization is not a concern in these injection-moulded and annealed nylon 6/nylon 6IcoT blends.

CONCLUSIONS

Injection-moulded nylon 6/nylon 6IcoT blends are homogeneous, but metastable. Phase separation occurred when the as-moulded samples were annealed due to entropic effects from crystallization and differences in chain conformation and stiffness. Transamidization was insignificant and did not affect the phase behaviour. Blending nylon 6IcoT with nylon 6 enhanced the crystallization of the nylon 6 component after annealing, which could be due to fewer tie molecules in the blend. Microcrystals formed during annealing and their melting temperature and melting energy were composition-dependent, probably because their size and structure were composition-dependent.

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REFERENCES

1 Chu, C. and Berner, B. *J. Appl. Polym. Sci.* 1993 **47,** 1083

2 Hseih, D. T. and Peiffer, D. G. *J. Appl. Polym. Sci.* 1993, **47,** 1469

3 Yee, A. F. *Polym. Eng. Sci.* 1977, **17,** 213

4 Sue, H. and Yee, A. F. *J. Mater. Sci.* 1989, **24,** 1447

5 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953

6 Aubin, M. and Prud'homme, R. E. *Macromolecules* 1980, **13,** 3655

7 Zhou, Z. L. and Eisenberg, A. *J. Polym. Sci., Phys. Edn.* 1983, **21,** 595

8 Kekufuta, F., Shimizu, H. and Nakamara, J. *Macromolecules* 1981, **14,** 1178

9 Cruz, C. A., Barlow, J. W. and Paul, D. R. *Macromolecules* 1979, **12,** 726

10 Bates, F. S., Schulz, M. F., Rosedale, J. H. and Almdal, K. *Macromolecules* 1992, **25,** 5547

11 Barlow, J. W. and Paul, D. R. *Polym. Eng. Sci.* 1981, **21,** 985

12 Liu, A. J. and Fredrickson, G. H. *Macromolecules* 1992, **25,** 5551

13 Cifra, P., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1988, **21,** 446

14 Howe, S. E. and Coleman, M. M. *Macromolecules* 1986, **19,** 72

15 Bates, F. S. and Fredrickson, G. H. *Macromolecules* 1994, **27,** 1065

16 Wang, H. H. and Lin, M. F. *J. Appl. Polym. Sci.* 1991, **43,** 259

17 More, D. R. and Mathias, L. J. *J. Appl. Polym. Sci.* 1986, **32,** 6299

18 Takayanagi, M., Ogata, T., Morikawa, M. and Kai, T. *J. Macromol. Sci.* 1980, **B17,** 591

19 Lilaonitkul, A., West, L. C. and Cooper, S. L. *J. Macromol. Sci.* 1976, **B12,** 563

20 Ellis, T. S. *Polymer* 1988, **29,** 2015

21 Prud'homme, R. E. *Polym. Eng. Sci.* 1982, **22,** 1138

22 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8,** 909

23 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979

24 Jo, W. H. and Baik, D. H. *J. Polym. Sci.* 1989, **B27,** 673

25 Kekufuta, F., Shimizu, H. and Nakumura, J. *Macromolecules* 1981, **14,** 1178

26 Gaur, U., Lau, S., Wunderlich, B. B. and Wunderlich, B. *J. Phys. Chem. Ref. Data* 1983, **12,** 88

27 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **1,** 123

28 Gordon, M. and Taylor, J. S. *J. Appl. Chem.* 1952, **2,** 495

29 'Encyclopedia of Polym. Sci. Eng.', Vol. 11, John Wiley, New York, 1985

30 Struik, L. C. C. *Polymer* 1987, **28,** 1521

31 Khanna, Y. P. *J. Appl. Polym. Sci.* 1990, **40,** 569

32 Khanna, Y. P., Turi, E. A. and Sibilia, J. P. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22,** 2175

33 Wunderlich, B. 'Macromolecular Physics', Vol. 3, Academic Press, New York, 1980

34 Li, W. and Prud'Homme, R. *J. Polym. Sci., Polym. Phys. Edn.* 1993, **31,** 719

35 Ellis, T. S. *Macromolecules* 1991, **24,** 3845

36 Ellis, T. S. *Macromolecules* 1990, **23,** 1494

37 Ellis, T. S. *Macromolecules* 1990, **23,** 2807

38 Hahn, B., Wendorff, J. H. and Yoon, D. Y. *Macromolecules* 1985, **18,** 718

39 Hahn, B. R., Hermann-Schonher, O. and Wendorff, J. H. *Polymer* 1987, **28,** 201

40 Ando, Y. and Yoon, D. Y. *Am. Chem. Soc. Polym. Prepr.* 1988, **29,** 381

41 Kumar, S. K. and Yoon, D. Y. *Macromolecules* 1989, **22,** 4098

42 McDonnell, M. Private communication, 1994

43 Takeda, Y. and Paul, D. R. *Polymer* 1991, **32,** 2771