Mixing relationships in aliphatic polyamide blends

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The correlation of chemical composition and phase phenomena of polyamide blends has now been extended to binary aliphatic polyamide blends. The close similarity of structure and chemico-physical properties has usually made such an identification extremely difficult. This has now been overcome to a large extent by implementing enthalpy recovery measurements as the analytical procedure. It has been determined that, with the exception of blends of nylon 6 containing nylon 66, binary aliphatic polyamide blends will initially form phase-separated systems. This is in agreement with theoretical arguments based upon the dominant role of unfavourable interactions in polyamide blends. The nylon 6/nylon 66 blend represents the athermal condition, which coupled with the inability to detect any heterogeneity, suggests this blend may be homogeneous on a molecular scale. It has also been shown that in some instances transreaction in the melt can proceed rapidly during short periods of exposure to high temperature, e.g. 310°C for 4 min, with the formation of miscible blends. These observations are also reconciled qualitatively with theoretical considerations.

(Keywords: aliphatic polyamide blends; enthalpy recovery; miscibility; transreaction)

INTRODUCTION

Binary blends of common aliphatic polyamides have been examined in various contexts on a number of occasions[1-4]. Solvent cast blends of nylon 6 and nylon 12 provided evidence of phase separation[2], while in contrast, dynamic mechanical measurements[4] of nylon 6 blends containing nylon 66 indicated behaviour consistent with miscibility. However, close inspection of the available literature confirms that a complete description of phase behaviour within this category of blends has yet to emerge. This situation has arisen in part due to the close similarity of structure and chemico-physical properties of the polymers involved, which has in the past rendered most analytical techniques ineffectual in addressing the question with complete confidence. These difficulties have now been circumvented to a large extent by the application of a thermoanalytical technique involving enthalpy recovery measurements[5]; a procedure that was developed recently specifically to overcome this kind of problem. A number of studies[6-10] have provided ample evidence to illustrate the effectiveness of this technique for a diverse selection of polymer blends. Moreover, the information contained in this communication will also illustrate the utility of the procedure where the added complication of crystallinity has been introduced.

In addition to the above, a series of recent articles[6,11-14] has devoted much attention to investigating the factors controlling phase behaviour in mixtures of aliphatic and aromatic polyamides. An important feature within these discussions was the question of phase behaviour of binary aliphatic polyamide blends. A simple approximation founded upon the intramolecular repulsion model[15-17] indicated that phase separation should be the dominant behaviour. The data presented here will confirm that this is indeed the prevalent equilibrium behaviour by reference to studies of nylon 46/nylon 6, nylon 6/nylon 66 and nylon 66/nylon 612 blends, respectively. The choice of blends has been designed to represent the spectrum of polyamide polarity, ranging from nylon 46 to the more polyethylene-like nylon 612. The blend of nylon 6 containing nylon 66 is a special test case which, under the present theoretical scheme, constitutes the athermal condition. Accordingly it will be shown that the theoretical and practical issues concerning phase phenomena for this blend are considerably more difficult to resolve.

EXPERIMENTAL

Materials

The polymers nylon 6, nylon 46, nylon 66 and nylon 612 were supplied as Zytel 211 (DuPont), Stanyl (Allied), Zytel 101 (DuPont) and Zytel 151 (DuPont), respectively. A summary of their composition and properties is presented in *Table 1*. Values given for M_n and M_w were obtained by size exclusion chromatography (s.e.c.) relative to polystyrene standards and should, therefore, be viewed only for comparative purposes.

Procedures

Blend preparation was performed by coprecipitation from a common solvent in the manner described previously[11-13]. Pure polymers were subjected to an identical preparative procedure in order to establish a uniform point of origin. Thermal characterization of the blends, together with the pure polymers, was achieved by using enthalpy recovery measurements following procedures described in more detail in the literature[5,6]. Briefly, this was effected by using a Perkin-Elmer differential scanning calorimeter at a heating rate of 20°C min^{-1}. The parameters T_{ons}, the onset of the

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Table 1 Structure and properties of the polymers

Polymer	Structure	T_g (°C)	T_m (°C)	ΔC_p (J g^{-1} K^{-1})	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
Nylon 46 (Stanyl)	$\left[\begin{matrix}H & O & & O & H\\ | & \| & & \| & |\end{matrix}\right.$ $-(CH_2)_4-N-C-(CH_2)_4-C-N-\Big]_n$	59	291	0.19	22	100
Nylon 6 (Zytel 211)	$\left[\begin{matrix}H & O\\ | & \|\end{matrix}\right.$ $-(CH_2)_5-N-C-\Big]_n$	48	223	0.20	61	87
Nylon 66 (Zytel 101)	$\left[\begin{matrix}H & O & & O & H\\ | & \| & & \| & |\end{matrix}\right.$ $-(CH_2)_6-N-C-(CH_2)_4-C-N-\Big]_n$	52	262	0.17	31	93
Nylon 612 (Zytel 151)	$\left[\begin{matrix}H & O & & O & H\\ | & \| & & \| & |\end{matrix}\right.$ $-(CH_2)_6-N-C-(CH_2)_{10}-C-N-\Big]_n$	35	219	0.17	15	66

recovery peak, T_{max}, the maximum of the peak, h_r (W g^{-1}), the height of the peak, t_a (min) the ageing time, and ΔH_D (J g^{-1}), the enthalpy difference between aged and unaged samples, are the same as those defined previously[5,6]. The value obtained for T_g in *Table 1* was also obtained at a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

The primary concern was to establish behaviour in blends formed in the absence of contaminating thermal processes, such as transreaction[18]. Several studies[11,19] have indicated that for those polyamide blends that exist in a marginal immiscible phase condition, exposure to high temperature for only short periods of time is sufficient to promote an apparent totally miscible state. The method of blend fabrication, by coprecipitation from a common solvent, produces an intimately mixed system, but one that is in a non-equilibrium state. Therefore, when blends of crystalline polymers are involved it is necessary to establish equilibrium by melting all the species present. This procedure was applied to all the blends, but because of the misleading potential of transreaction in the melt only a short time of exposure (1 min) at high temperature was allowed. Thus for the nylon 6/nylon 46 blend, the sample was annealed at 230°C for 2 min, then exposed to 300°C for 1 min, before being cooled down at 20°C min^{-1} before analysis. Unless stated otherwise all blends investigated were prepared on a 50% w/w compositional basis. It will be assumed that this approximates the minimum of the cloud-point curve for phase separation and, therefore, represents the composition at which phase separation would be most likely to occur.

Nylon 6/nylon 46

There is no information currently available in the literature concerning the blending behaviour of nylon 46 with other semicrystalline polyamides. The T_gs of the pure polymers were measured as 59°C (nylon 46) and 48°C (nylon 6). An eleven degree separation of T_gs, in a blend containing only amorphous polymers, is sometimes sufficient to obtain information on phase behaviour; if not by conventional analysis, then certainly by more refined procedures[5]. In blends of semicrystalline polyamides the ability to analyse phase behaviour is further complicated by additional factors such as a small incremental change of heat capacity, ΔC_p, at T_g. For the nylon 46/nylon 6 blend, this is approximately one-half ($\simeq$0.2 J g^{-1} K^{-1}, cf. *Table 1*) of that of a completely amorphous polyamide ($\simeq$0.4 J g^{-1} K^{-1} (ref. 6)). In addition to this, there is a broad range of temperature over which T_g occurs (30–40°C for nylon 6 compared with 15–20°C for a completely amorphous polyamide). The observations described above combine to produce rather featureless thermograms, as can be seen in *Figure 1*. The onset T_g of the blend approximates to that of pure nylon 6 and, although this may suggest immiscibility, the uniform transition provides no additional evidence to support this.

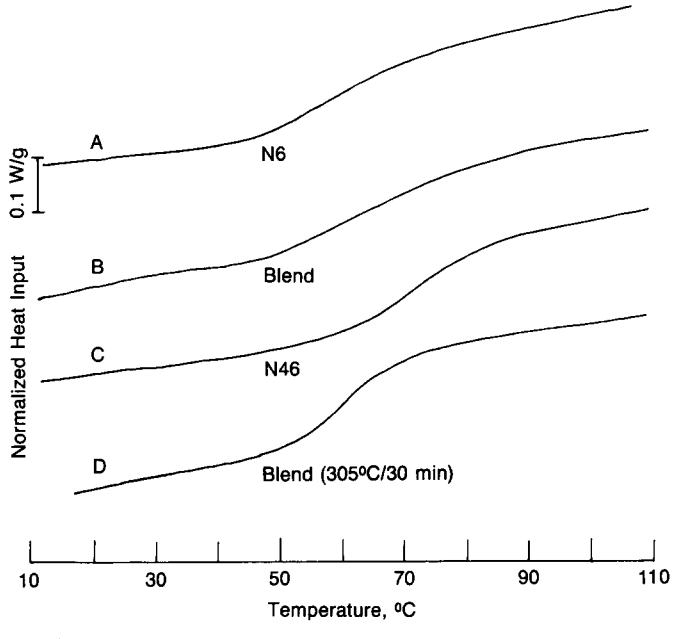

Figure 1 Representative thermograms of unaged polymers and blends: A, nylon 6; B, nylon 6/nylon 46 (50%); C, nylon 46; D, nylon 6/nylon 46 (50%) subjected to 305°C for 30 min

Enthalpy recovery measurements, at an annealing temperature T_a = 50°C, shown in *Figure 2*, provide the necessary evidence to conclude that these two polymers are immiscible, or that a heterogeneous amorphous phase is present. Although only one recovery peak of a heterogeneous nature was produced, the T_{max} of the blend is coincident with that of pure nylon 46, whereas T_{ons} identifies with pure nylon 6. Further analysis at T_a = 40°C provided supporting data for phase separation, as can

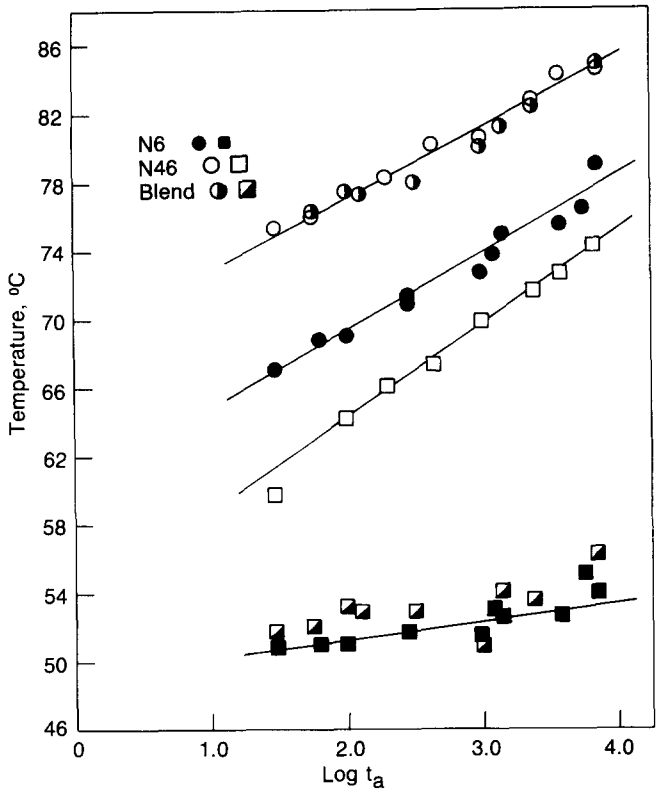

Figure 2 Enthalpy recovery kinetics of nylon 6, nylon 46 and a nylon 6/nylon 46 (50%) blend (T_a = 50°C): T_{max}, circles; T_{ons}, squares

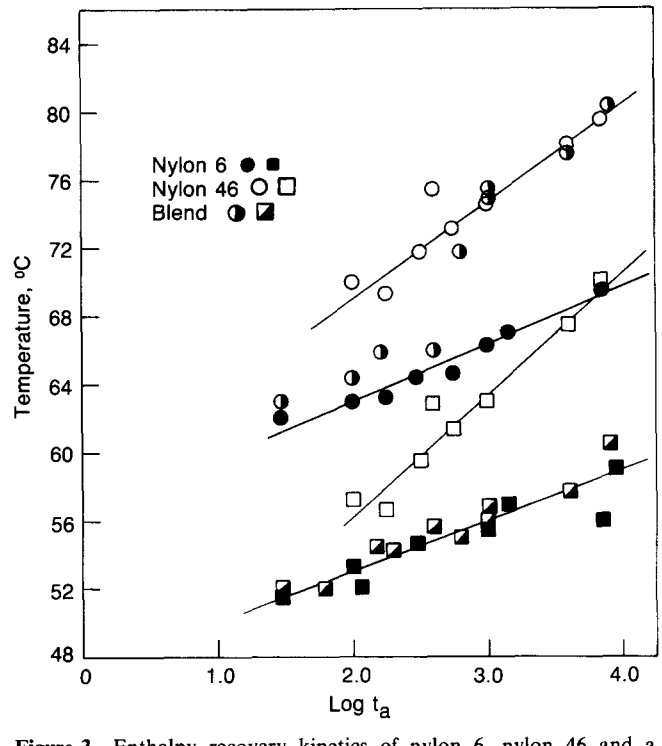

Figure 3 Enthalpy recovery kinetics of nylon 6, nylon 46 and a nylon 6/nylon 46 (50%) blend (T_a = 40°C): T_{max}, circles; T_{ons}, squares

be seen in *Figure 3*. At this temperature, however, at low values of log t_a, T_{max} in the blend is dominated by the nylon 6 phase. At higher ageing times, the nylon 46 phase develops a more pronounced recovery peak, which correlates with that of pure nylon 46. Again T_{ons} is coincident with that of pure nylon 6. Measurements of h_r complement the behaviour noted above. At T_a = 50°C, the nylon 46 has considerably larger values of h_r over the complete range of log t_a (see *Figure 4*). Accordingly, this recovery peak dominates the phase-separated blend as shown in *Figure 2*. When T_a = 40°C (*Figure 5*) the two pure polymers reveal similar values of h_r over the whole range of log t_a. This behaviour is then reflected in the switch of T_{max} in the blend, as noted previously in *Figure 3*. Values of h_r recorded for the blend indicate an approximate average of two separate peaks superimposed one upon the other. This is particularly evident in *Figure 5*, which illustrates a much-reduced peak height in the

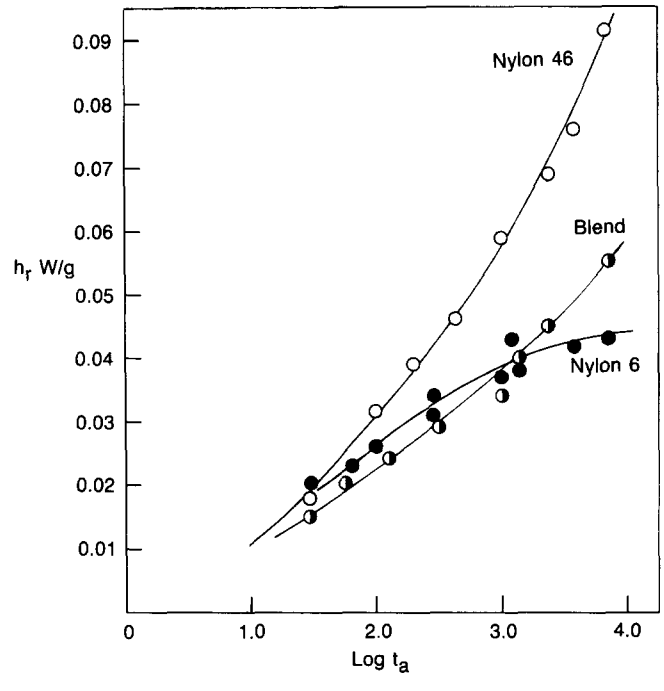

Figure 4 Recovery peak height of nylon 6 (●), nylon 46 (○) and a nylon 6/nylon 46 (50%) blend (◑) at T_a = 50°C

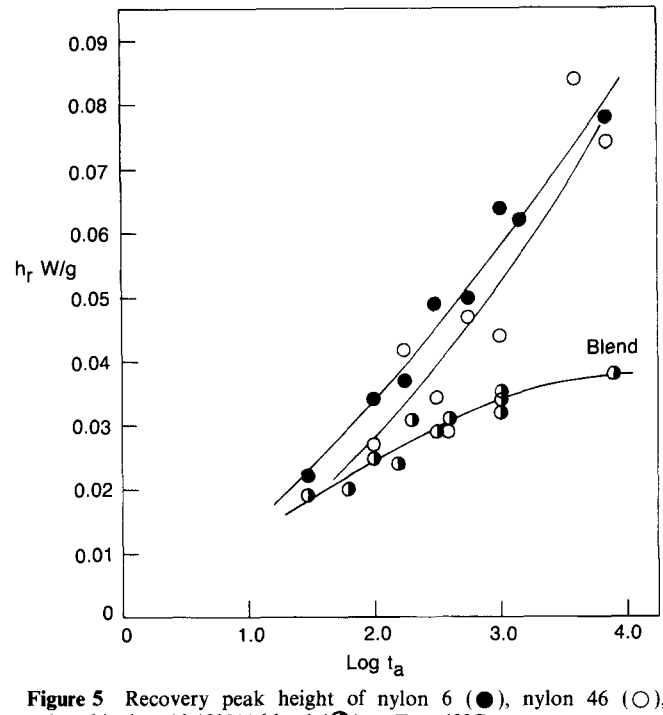

Figure 5 Recovery peak height of nylon 6 (●), nylon 46 (○), nylon 6/nylon 46 (50%) blend (◑) at T_a = 40°C

blend compared to that of the two pure polymers. Indeed, in many instances, and particularly at higher values of log t_a, the subtracted thermograms were seen to comprise two closely separated peaks.

Measured values of the enthalpy difference between aged and unaged samples are shown in *Figure 6*. There is some scatter in the data, but it should be remembered that values are approximately one-half of those measured for completely amorphous polyamides[6], which obviously increases the experimental error. The data show very little contrast both with respect to blend composition and annealing temperature. Although this observation provides little information in itself, it does confirm a valid interpretation of measured values of h_r, since the level of crystallinity, and therefore proportion of amorphous material, can be considered to be approximately the same in both the blends and the pure polymers.

A recent study[20] has concluded that crystallization in miscible semicrystalline/amorphous polyamide blends can induce phase segregation leading to a heterogeneous mixed amorphous phase. It follows therefore that if the same morphological development occurred in a miscible blend of nylon 46/nylon 6 then it could be argued that the data shown in *Figures 2–6* could represent this particular situation. Presently, it is believed that the experimental observations correlate so closely to a two-phase system that this does not occur.

Nylon 66/nylon 612

Many of the concerns described in the preceding sections apply with equal importance to the investigation of the blend of nylon 612 and nylon 66. The blend was treated at 235°C for 2 min followed by 275°C (≃10°C above the melting point for nylon 66) for 2 min before cooling at 20°C min^{-1}. In many previous studies[11–13] it has been noted that 2 min above the melting point of a crystallizable polymer has been sufficient to induce complete phase separation within an inherently immiscible

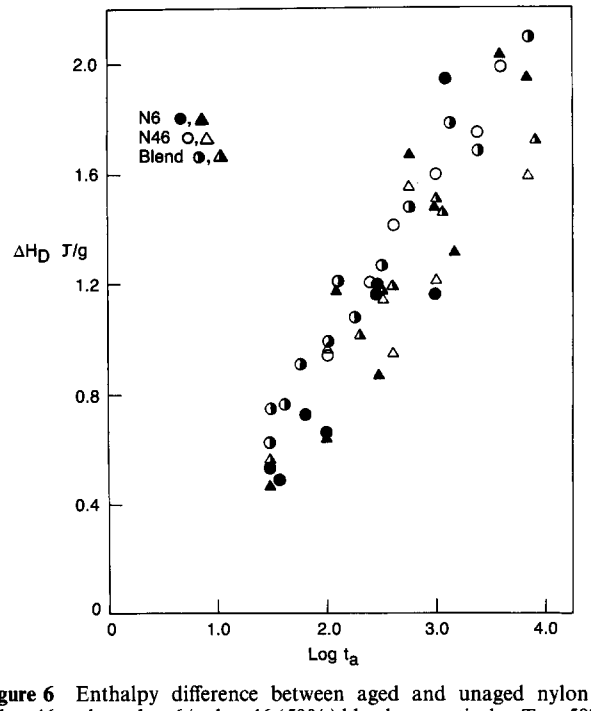

Figure 6 Enthalpy difference between aged and unaged nylon 6, nylon 46 and a nylon 6/nylon 46 (50%) blend, respectively: T_a = 50°C, circles; T_a = 40°C, triangles

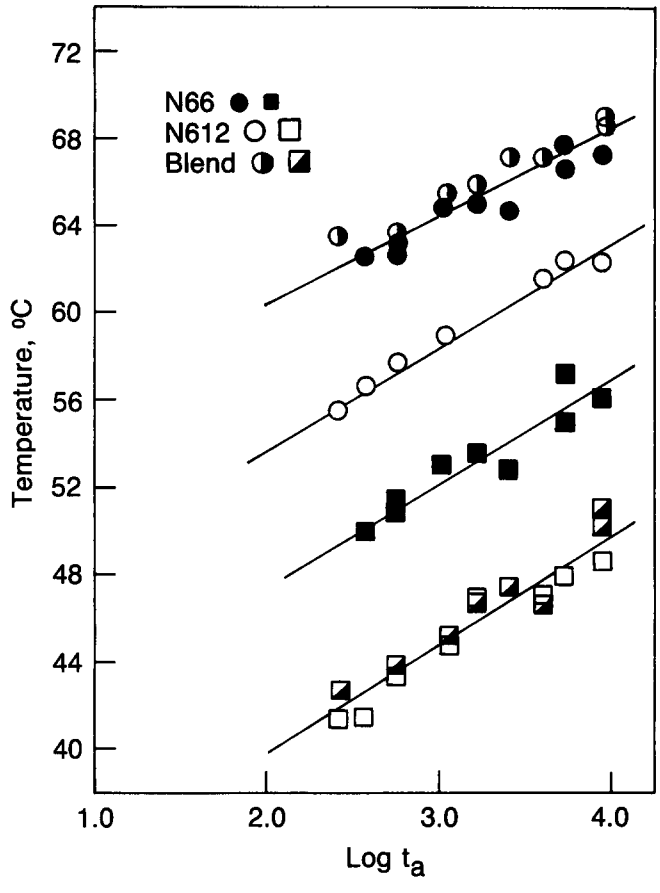

Figure 7 Enthalpy recovery kinetics of nylon 66, nylon 612 and a nylon 66/nylon 612 (50%) blend (T_a = 30%): T_{max}, circles; T_{ons}, squares

blend. The presence of a 17°C separation of the T_gs of the pure components was still insufficient to produce any characteristic features in the thermogram that could be ascribed to a particular identifiable phase phenomenon. A broad T_g with an onset of approximately 35°C is indicative, but not conclusive, of the presence of a pure nylon 612 phase. Enthalpy recovery measurements were again found to provide considerable detailed evidence to support the formation of a phase-separated blend. This is illustrated in *Figures 7–9*. An ageing temperature T_a = 30°C was chosen because of the lower T_g of nylon 612 (35°C) compared with that of nylon 66 (52°C). Although only a single recovery peak was observed in the blend, T_{max} was found to identify with pure nylon 66 and T_{ons} was found to be coincident with that of pure nylon 612 (see *Figure 7*). The position of T_{max} in the blend is slightly unexpected when viewed in relation to the data shown in *Figure 8*, which indicates that nylon 612 develops a marginally higher recovery peak. As before, the peak recovery height in the blend is significantly reduced in stature owing to phase separation. This is also illustrated in *Figure 9*, which contrasts the thermograms of the pure polymers and the blend when log $t_a \simeq 3.94$. Although not shown, measurements of the enthalpy difference between aged and unaged samples of the blend and pure polymers were qualitatively and quantitatively the same as those described previously for blends of nylon 46 and nylon 6 (*Figure 6*).

Nylon 6/nylon 66

The chemical, structural and physical similarity of nylon 6 and nylon 66 present a demanding test for any

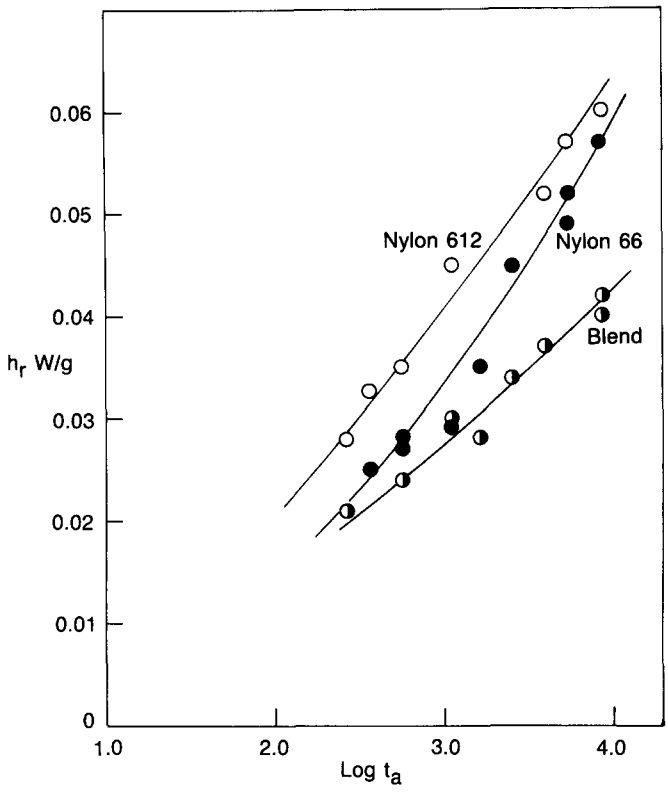

Figure 8 Recovery peak height of nylon 66, nylon 612, and a nylon 66/nylon 612 (50%) blend (T_a = 30°C)

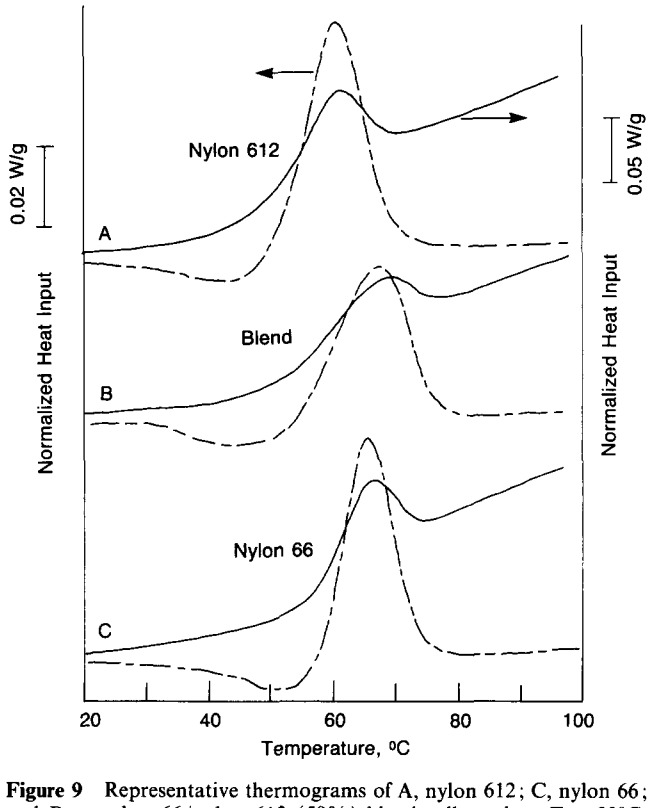

Figure 9 Representative thermograms of A, nylon 612; C, nylon 66; and B, a nylon 66/nylon 612 (50%) blend; all aged at T_a = 30°C, log t_a = 3.94 (subtraction of aged and unaged thermograms are also shown — · —)

analytical procedure to characterize blends of these polymers. The T_gs of the pure polymers (nylon 6, 48°C; nylon 66, 52°C) and the blends are extremely close, as illustrated in *Figure 10*. There appears to be a gradual progression of T_g to that of nylon 66 as the nylon 66 content increases, but the transitions are once again rather featureless.

Enthalpy recovery kinetics at T_a = 40°C and T_a = 50°C are shown in *Figures 11* and *12*. The data presented indicate that a 50 : 50 blend is approximately intermediate

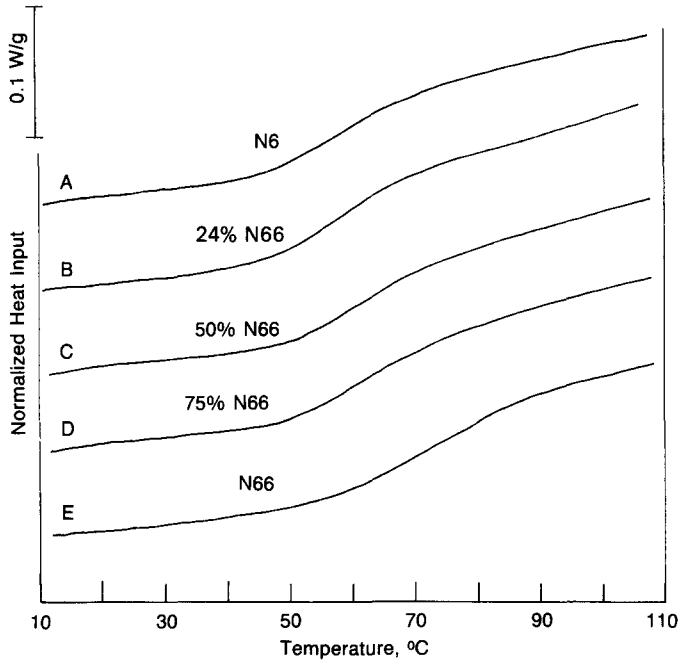

Figure 10 Representative thermograms of unaged polymers and blends: A, nylon 6; B, nylon 6/nylon 66 (24%); C, nylon 6/nylon 66 (50%); D, nylon 6/nylon 66 (75%); E, nylon 66

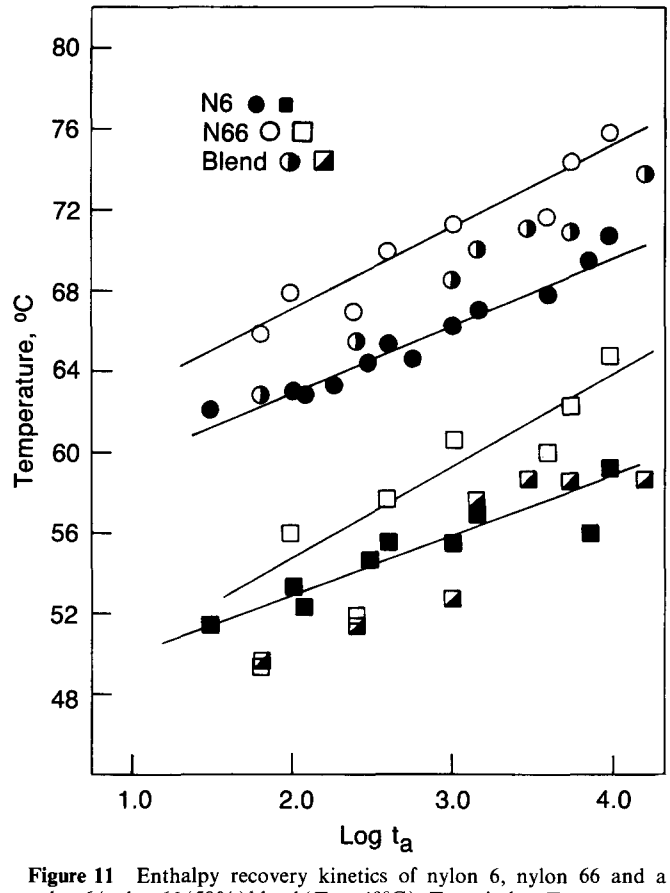

Figure 11 Enthalpy recovery kinetics of nylon 6, nylon 66 and a nylon 6/nylon 66 (50%) blend (T_a = 40°C); T_{max}, circles; T_{ons}, squares

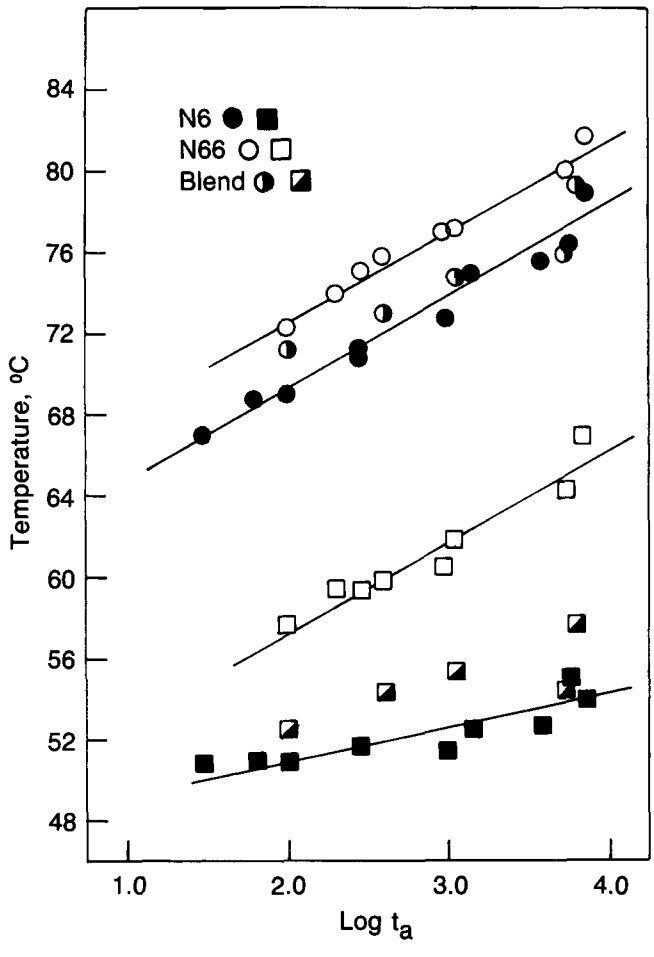

Figure 12 Enthalpy recovery kinetics of nylon 6, nylon 66 and a nylon 6/nylon 66 (50%) blend (T_a = 50°C): T_{max}, circles; T_{ons}, squares

between that of the pure polymers, particularly with respect to values of T_{max}. There is considerable scatter in the data obtained for T_{ons} and it is difficult to derive any firm conclusions from these measurements. Measurement of T_{ons} is more prone to error because of its inherent subjectivity and in general T_{max} is the more discriminating parameter of the two. This is still true in the situation shown in *Figure 12*, where the difference between the pure polymers is greater for T_{ons} than that measured for T_{max}. Individual thermograms, as well as subtracted thermograms, were symptomatic of homogeneous materials, but two recovery peaks separated by only a few degrees may also have produced such an effect.

Recovery measurements were extended to blends containing 24% and 75%, respectively, of nylon 66 in an attempt to detect any heterogeneity. It was suspected that a phase-separated blend containing unequal amounts of each polymer may develop recovery peaks that identified with the respective pure polymer present in the blend as the major component. The data obtained from these blends is compared with that obtained from the pure polymers, as shown in *Figure 13*. Again, values obtained for T_{ons} are rather inconclusive, but the T_{max} data signifies intermediate behaviour, particularly at the higher values of log t_a. Under these conditions a progressive increase of T_{max} towards that of pure nylon 66 was noted as the content of this component in the blend increases.

Measured values of h_r and ΔH_D for all the blends are summarized in *Figures 14* and *15*. The information presented provides no further assistance in elaborating on the behaviour described thus far. There is a large degree of scatter, which is exaggerated by the sensitive scale; a standard error has not been determined but it is believed to be of the order of approximately ±10%. In summary, however, all of the data obtained reveal no suggestion of a phase-separated blend, although it cannot be stated positively that a miscible blend has been formed.

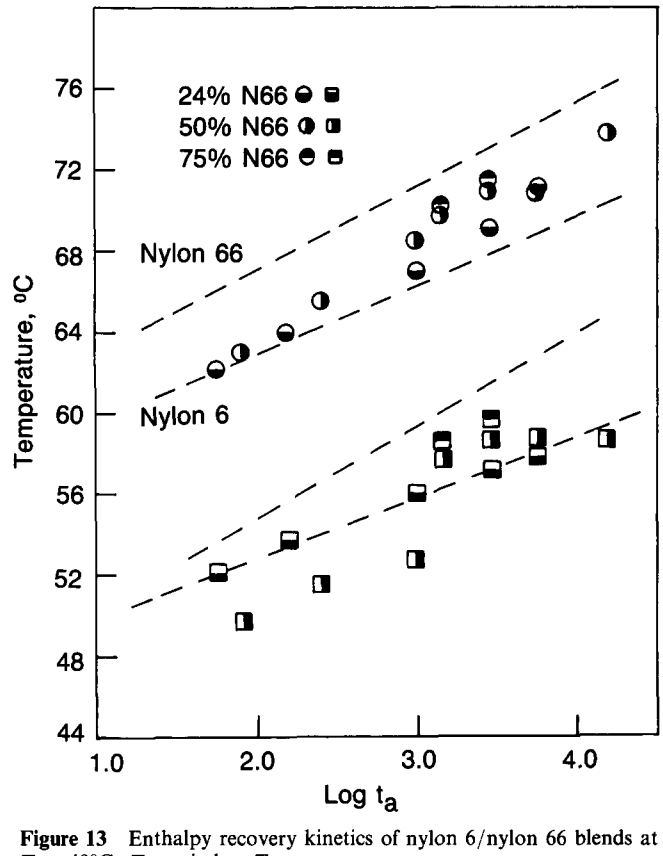

Figure 13 Enthalpy recovery kinetics of nylon 6/nylon 66 blends at T_a = 40°C: T_{max}, circles; T_{ons}, squares

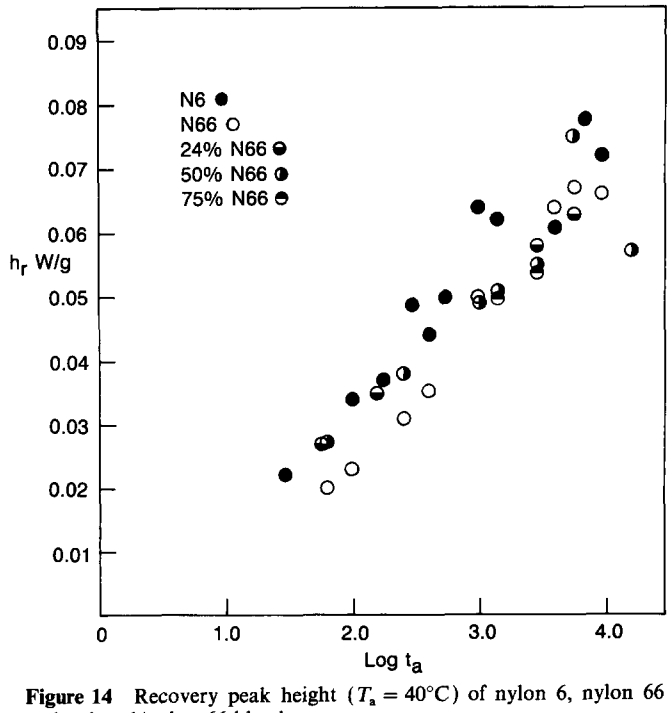

Figure 14 Recovery peak height (T_a = 40°C) of nylon 6, nylon 66 and nylon 6/nylon 66 blends

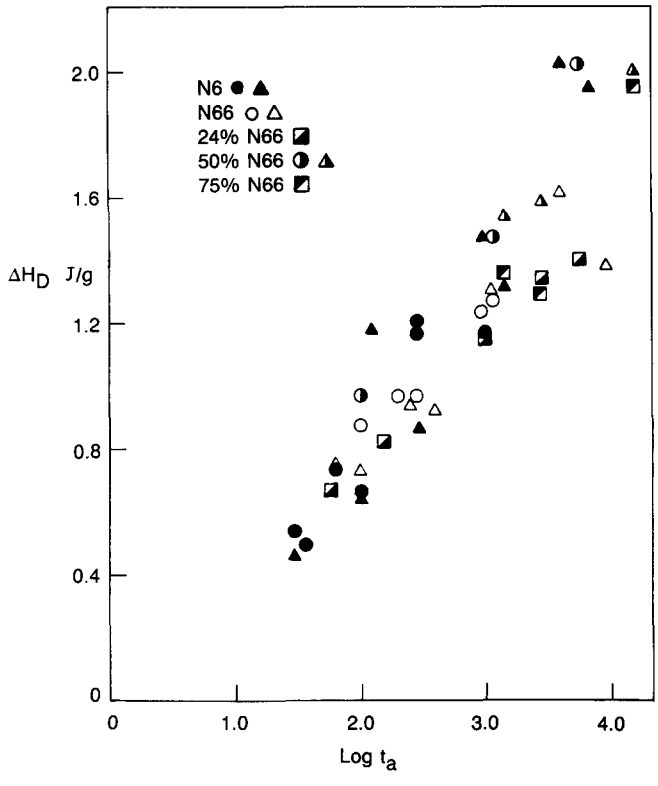

Figure 15 Enthalpy difference between aged and unaged nylon 6, nylon 66 and blends: $T_a = 50°C$, circles; $T_a = 40°C$, squares

The question of transreaction

Transamidation in the melt in polyamide blends is well documented in the literature[18,19], but the extent to which it occurs in the blends described here will depend upon time, temperature and the degree to which individual species come into contact with each other. With regard to the primary concern, stated earlier, that for characterization purposes it should be excluded as much as possible, it is believed that this was largely achieved. However, separate experiments were conducted to include a brief survey of its consequences on blend phase behaviour.

As described previously, a blend of nylon 6 and nylon 46 in a pristine condition is phase-separated. However, subjecting the 50:50 blend to 310°C for 4 min results in a homogeneous mixed amorphous phase. This is illustrated in *Figure 16*, which shows a heterogeneous recovery peak (thermogram B) transformed to one (thermogram D) comparable to that of the pure polymers. Not only is its measured value of h_r similar to that of the pure polymers, but also the position of T_{max} and T_{ons} typifies that of a miscible blend. Consequently, at $\log t_a \simeq 3.9$, and the value of h_r of the phase-separated blend, 0.038 W g^{-1}, increases to 0.082 W g^{-1}. This is also accompanied by a slight increase of ΔH_D from 1.7 J g^{-1} to 2.0 J g^{-1}, indicative of a slight increase of the amorphous fraction. Measured values of ΔC_p also increase to 0.23 J g^{-1} K^{-1} from approximately 0.19 J g^{-1} K^{-1}. These observations have been attributed to the presence of transreaction in the melt, promoting the development of a miscible mixed amorphous phase. This is also supported by thermogram D in *Figure 1*, which describes an abrupt transition that is unlike that of thermogram B; the unreacted blend transition. Apparently, transreaction occurs very rapidly under these conditions and it is highly probable that simple melt blending and processing of these two polymers would lead to a homogeneous, apparently miscible mixture. Separate crystalline domains with separate melting points would also be present since no evidence of cocrystallization was observed. Finally, it is of interest to note, that with regard to T_g, ΔC_p and enthalpy recovery, continued heating for extended periods of time (30 min) induces little further change (see *Figure 1*).

Because of poor resolution of the nylon 66/nylon 6 blend behaviour no transreaction experiments were conducted. However, prolonged heating of a 50:50 blend of nylon 612/nylon 66 blend revealed complementary, but significantly different, behaviour to that of nylon 46/nylon 6. A blend exposed to 300°C for 5 min possessed a recovery peak comparable to that of the phase separated blend, e.g. at $\log t_a = 3.73$, $T_{max} = 67.2°C$ and $h_r = 0.44$ W g^{-1}; cf. 67.4°C and 0.44 W g^{-1}. Continued heating at 300°C for 15 min produced a recovery peak characteristic of a single-phase system intermediate between that of the two polymers, e.g. at $\log t_a = 3.45$, $T_{max} = 61.6°C$, $h_r = 0.54$ W g^{-1}. This is again consistent with transreaction in the melt, which when judged at a subjective level appears to occur less rapidly than that noted for nylon 46 and nylon 6. Qualitative reasons to account for this difference will be proposed shortly.

Comparison of experiment and theory

The introductory comments have alluded to the judicial choice of the blends investigated. The theoretical arguments for investigating these specific binary aliphatic polyamide blends are founded upon earlier discussions[11,13]. Briefly, phase behaviour in blends of this nature is indicated by the value of χ_{blend}, an effective interaction parameter, which as a first approximation signifies

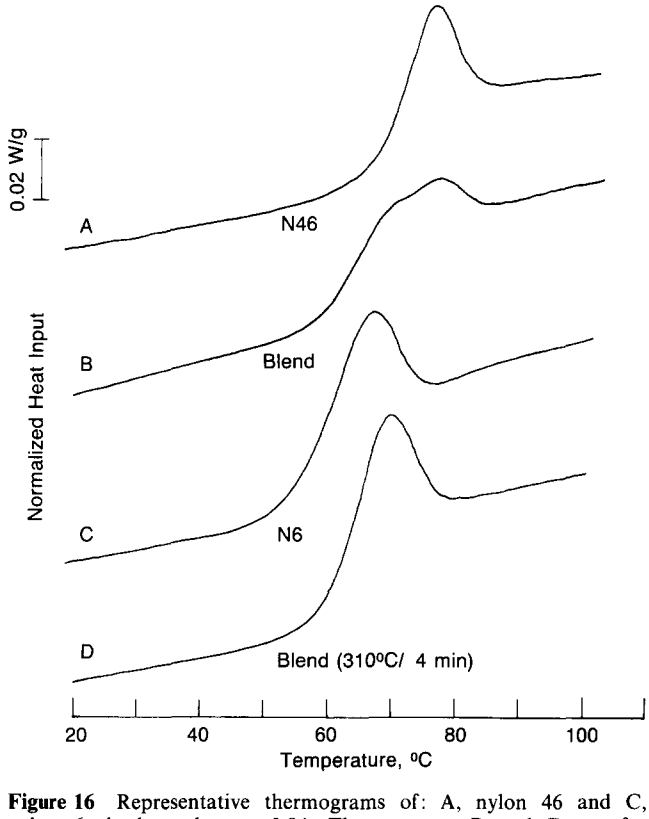

Figure 16 Representative thermograms of: A, nylon 46 and C, nylon 6; both at $\log t_a = 3.84$. Thermograms B and D are for nylon 6/nylon 46 (50%) blend at $t_a = 3.91$. Thermogram D represents a transreacted blend (310°C/4 min)

miscibility ($\chi_{blend} < 0$) or immiscibility ($\chi_{blend} > 0$). In binary aliphatic polyamide blends, treated as A_xB_{1-x}/A_yB_{1-y} copolymer blends, where A and B represent methylene and amide groups, respectively, and x and y are mer volume fractions, then χ_{blend} is given by[11]

$$\chi_{blend} = (x - y)^2 \chi_{AB} \quad (1)$$

χ_{AB} is the segmental interaction parameter, $\chi_{AB} = 7.984$[13], such that as a first approximation χ_{blend} is always positive for binary aliphatic polyamide blends and predicts the formation of a phase-separated system. This result presents an interesting paradox if the intuitive argument is proposed that blends of this nature are capable of engaging in specific interactions in the form of hydrogen bonding; a feature commonly proposed as a necessary requirement for miscibility. It may be argued that the blend components chosen for this study do not meet the structural requirements necessary for sufficient hydrogen-bonding interactions to occur. For example, Brisson and Breault relied[21] upon a precise description of configurational and conformational requirements to depict hydrogen-bond-driven miscibility for certain aromatic polyamide blends. There is no information available to judge whether or not a similar analysis is capable of explaining the results described here.

By choosing nylon 6 and nylon 66 (x and $y = 0.7676$) as a point of reference, the blend of nylon 46/nylon 6 was chosen since it represents a blend with a component containing a higher volume fraction of amide units ($x = 0.7255$). The blend with nylon 66 and nylon 612 represents the opposite case of a blend component with a lower volume fraction of amide units ($x = 0.8409$). Both blends are predicted to be immiscible (nylon 46/nylon 6, $\chi_{blend} \simeq 0.014$; nylon 66/nylon 612, $\chi_{blend} \simeq 0.043$), a result that appears to be confirmed by the experimental data provided in earlier sections. It is also of interest to emphasize that χ_{blend} is closer to zero for the nylon 46/nylon 6 blend and under these circumstances the interface may be quite large when compared to the nylon 612/nylon 66 blend. Notwithstanding the current uncertainty in the scaling of model calculations, the thickness of the interface, d, is predicted to vary as $d \sim \chi^{-1/2}$ (ref. 22). Consequently, the increased level of contact between nylon 46 and nylon 6 species in the interface of the blend will promote more rapid transreaction in the melt when compared to that of the nylon 66/nylon 612 blend. This reasoning is verified in a qualitative manner by the observations noted previously, although this assumes that chemical reactivities of all species involved are identical for all the polymers. An analogous situation, involving a binary blend of amorphous aromatic polyamides, has been reported previously[11]. In that particular instance rapid transaction was also observed and correlated with a value of χ_{blend} close to zero.

Although nylon 6 and nylon 66 contain a configurational variation, the chemical constitution of each is identical and they both contain the same volume fraction of methylene and amide units. Therefore, from the current theoretical perspective this provides a special situation whereby in a mean-field approximation, an athermal blend, $\chi_{blend} = 0$, will result. A combinatorial entropy contribution to the free energy of mixing will favour miscibility, although equation-of-state contributions will counter this effect. Currently there is no information available to reliably quantify all of these terms and in conclusion there is no explicit theoretical position from which to judge the experimental observations. Previous studies have indicated that this particular blend may be miscible[4]. Enthalpy recovery measurements reported here also favour this interpretation. Perhaps it is possible to state with greater certainty that there is no evidence whatsoever that blends of nylon 6 and nylon 66 are phase-separated.

CONCLUSIONS

Enthalpy recovery characteristics of aliphatic polyamide blends have provided compelling evidence to suggest that phase separation is the dominant behaviour. This has been shown to be in accord with current theoretical arguments that describe phase behaviour of polyamide blends in terms of the intramolecular repulsion model. In cases where the components have approximately the same proportion of amide units, miscibility may be possible. One such example investigated here is the nylon 6/nylon 66 blend, which, when neglecting the chemical configuration differences, has components that are indistinguishable from each other. Unfortunately, the close chemical and physical similarity of these two polymers has made it impossible to provide a conclusive determination of phase behaviour. The results supporting these conclusions have been collected on blends that have had only limited exposure to high temperatures. Additional studies have shown that thermally induced chemical transreaction has the ability to change substantially the behaviour observed. Consequently, melt blending may produce entirely different conclusions concerning phase phenomena in these materials.

Finally, it should be noted that the ability of enthalpy recovery measurements to resolve phase phenomena in difficult systems has been further demonstrated. This communication illustrates for the first time the ability of this technique to provide unique information on semicrystalline materials.

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