Communications to the Editor

On the Miscibility of Blends of Nylon 66 and Poly(hexamethylene isophthalamide), Nylon 6I

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In a recent communication[1] it was asserted that for predicting miscibility in binary polyamide blends, both a “rule of thumb” and a binary interaction model (BIM) approach are useful for screening purposes and that there is no good method for predicting phase behavior of homopolyamide blends. Such a comparison and conclusion are contrary to the published information.[2−14] The BIM was adapted[15−17] originally to fit into Flory−Huggins polymer solution theory and has been applied successfully to a wide variety of blends including those in which so-called specific interactions are believed to be responsible for producing miscible blends. For polyamide blends, it has been shown to describe copolymer and homopolymer blends and can be adjusted to account for configurational[10,13,14] and isomeric differences.[7,9] In view of the published information, it is not clear why the authors arrive at this conclusion and make the distinction between copolymers and homopolymers. These and other shortcomings make it necessary to clarify some of the issues concerning phase behavior of polyamide blends and highlight some of the problems involved with the preparation and characterization of semicrystalline/amorphous polyamide blends.

The “rule of thumb” noted above was derived from a single study[18] involving a miscibility window for blends of poly(*m*-phenylene isophthalamide) (Nomex or mPI) in poly(*n*-alkylisophthalamide)s. Briefly, it states that for binary polyamide blends an equality of carbon atoms between the blend constituents must exist for miscibility to occur. The breakdown of this rule was noted in the subsequent study,[1] and in view of the large body of published data which does not support this and the restrictive example from which it was deduced, it may be argued that the observations hardly qualify to be termed a “rule of thumb”. This apart, it was recognized that the real situation requires a more informed analysis and that amide group spacing is the fundamental basis for determining miscibility in polyamide blends. Although, it is argued, that other factors are involved, the latter is important in allowing for hydrogen-bonding interactions to promote miscibility. This view has persisted from a single earlier study and is an unbalanced conclusion when compared with the published data. Nylon 6I has been shown to be miscible[7] with nylon 6, nylon 66, nylon 69 (partial miscibility), and importantly random copolyamides of cyclic lactams of chemical composition which fit within a range dictated only by their overall methylene group content. Nylon 610, nylon 612, nylon 12, and copolyamides outside of this composition range are not miscible. A similar observation[7] has also been noted for several random aromatic copolyamides of very different chemical composition. This provides emphatic evidence that the amide group concentration and not their relative spacing determines phase behavior. Exceptions will inevitably occur, especially close to boundary conditions; however, the authors have ignored this fundamental observation in their criticism. Moreover, within the context of their hydrogen-bonding interpretation, it is difficult to perceive the commonality of microstructure that occurs in order to promote miscibility in the former group of polyamides that does not occur in the latter group.

In addition to the above, the study concludes that nylon 6,5 and nylon 6,9 become miscible with nylon 6I only after melting, without an investigation of how this may have occurred. Moreover, the conclusion that nylon 66 is immiscible with nylon 6I confuses the issue further. A part of this communication is directed to clarifying the experimental and analytical consequences of examining phase behavior of blends of this nature. It will be shown quite conclusively that conventional nylon 66 is miscible with nylon 6I in all proportions provided that the correct procedures are followed. It will also be shown how immiscibility may be concluded when the same blends are cast as a film from a solution of trifluoroacetic acid (TFA).

Experimental Section. The nylon 66 and nylon 6I involved in the studies described here are the same as those used previously.[2−8] The nylon 6I (structure confirmed by NMR) is an amorphous polymer and does not degrade to any measurable extent on short exposure to temperatures up to 280 °C. Films cast from trifluoroacetic acid (TFA) (99.7%) have been prepared in exactly the same manner as that described by Cote and Brisson.[1] Blends formed by precipitation using concentrated sulfuric acid (SA) (water precipitant) and trifluoroethanol/chloroform (TFE) (diethyl ether precipitant) solvents, respectively, have also been prepared.

The clear solutions of nylon 66, nylon 6I, and blends were cast as films and placed in a desiccator for 2 weeks. The nylon 66 became hazy, presumably due to crystallization, the nylon 6I remained clear, but the blends became considerably turbid, indicative of phase separation. Extensive drying (2 days) at 150 °C in a vacuum oven was found to be necessary in order to produce nylon 6I with a T_g consistent with its reported value. This is not a desirable “drying” protocol in the presence of an acid. The films were slightly brown after this process, and the blends were still turbid. During sample preparation using TFA, it was noted in several instances that turbid solutions were obtained during solvation. This occurred mainly when pellets of nylon 66 were used rather than reprecipitated nylon 66. Addition of more solvent failed to induce clarity, and spurious observations of turbidity were also obtained with a freshly received sample of 100% TFA. Although contamination by moisture cannot be ruled out, these observations tend to promote a lack of confidence in the ability of TFA to act in the prescribed manner. Only the clear solutions

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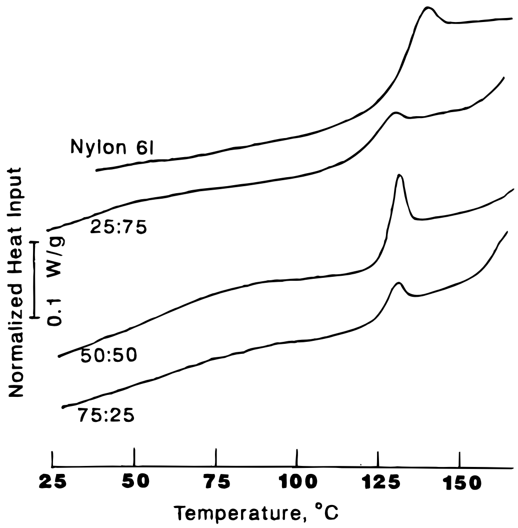

Figure 1. First heating cycle DSC thermograms of nylon 6I and blends (weight composition N 66:N 6I). Samples prepared as cast films from TFA. (Heating rate 20 °C/min).

Table 1. Thermal Properties of Nylon 66[a]/Nylon 6I Blends

	films cast from TFA		precipitated from solution	
blend comp (wt % nylon 6I)	$T_{\rm g}$ (°C) R1, R2[b]	ΔC_p (J/(g K)) R1, R2	$T_{\rm g}$ (°C)	ΔC_p (J/(g K))
100	121	0.38	118[c,d]	
75	117, 86	0.26, 0.4	93[d]	0.43
50	125, 51	0.35, 0.1	67[d]	0.45
			70[a] (SA)	0.43
25	123, 63	0.41, 0.19	55[d]	

[a] $T_{\rm g}$ of pure nylon 66 measured by DSC is 45 °C.[7] [b] R1,R2 = first and second heating cycles in DSC. [c] Reference 7. [d] Obtained at 10 °C/min heating rate.

were used in the study. It should also be noted that the mixed TFE/chloroform solvent system provided clear solutions exclusively.

An initial DSC analysis (first heating cycle) indicates behavior consistent with immiscibility across the whole range of composition. Thermograms presented in Figure 1 illustrate an almost pure separate nylon 6I phase whose $T_{\rm g}$ and normalized ΔC_p characteristics are recorded in Table 1. A repeat analysis, subsequent to melting and rapid cooling (DSC quench) of the blends, provided thermograms indicating that the blends containing 75% and 25% by weight, respectively, of nylon 6I were now miscible. The greatly reduced rate of crystallization of the nylon 66, which may be anticipated for a miscible blend containing 75% by weight of nylon 6I, allowed for a vitrified blend to be produced during the cooling cycle, a feature which also confirms the formation of a miscible blend. However, quench cooling in the calorimeter sample chamber is not particularly efficient and would still allow some or total crystallization in blends with a high nylon 66 content. The 50:50 blend still appeared to be heterogeneous. Although, some crystallization had occurred during cooling, the measured $T_{\rm g}$ is below that expected for a miscible blend (see Table 1).

The observations noted above indicate that although apparent phase separation during film casting does occur, only a short period of time (seconds) is required for some (or total) rehomogenization provided the constituents are in the liquid state.

If phase separation had occurred in the concentrated solution regime, during removal of solvent, the morphology developed would depend upon the local conditions. Nevertheless, the fact that film turbidity and primary DSC analysis indicate a heterogeneous mixture signifies that TFA is a questionable solvent for determining phase behavior of polyamide blends.

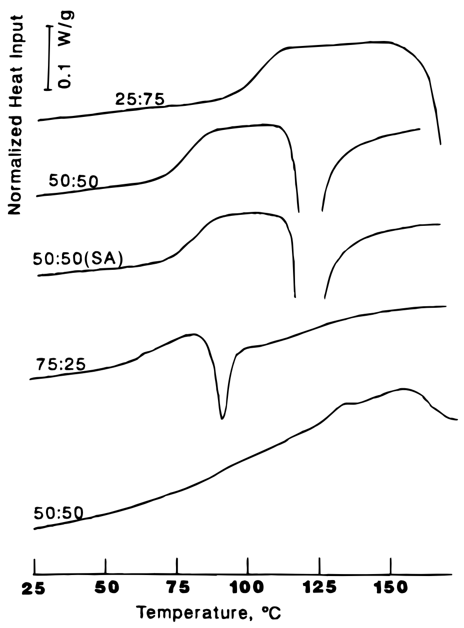

Figure 2. DSC thermograms of nylon 66/nylon 6I blends prepared by precipitation from TFE/chloroform solvent. Exception using SA as indicated.

Blends formed by precipitation gave the thermograms shown in Figure 2. These results and the information given in Table 1 indicate homogeneous blends across the whole range of composition irrespective of the solvent used. This is consistent with previous studies and confirms that nylon 66 and nylon 6I form miscible mixtures. All the thermograms shown in Figure 2 (except that noted) were obtained by exposure of a sample to the melt (275 °C) for less than 30 s and then plunged into liquid nitrogen. This is the most trivial method to efficiently quench cool samples and leads in most cases to complete vitrification. Even complete vitrification of the 75:25 blend is difficult owing to the still rapid rate of crystallization of nylon 66 in the blend.

The final thermogram in Figure 2 reveals the transformation of a 50:50 blend, prepared by precipitation, when annealed at 140 °C. The apparent heterogeneity is similar to those shown in Figure 1. This type of behavior is well documented[2,20] in similar crystalline/amorphous polamide blends and arises from the segregation of noncrystallizable species during crystallization of the nylon 66. It is a reversible phenomenon such that further melting and quenching cooling produce behavior identical to that shown in the thermograms in Figure 2.

If partial phase separation during solvent removal is not responsible for the apparent heterogeneity of nylon 66/nylon 6I blends, then the most likely reason for the thermograms shown in Figure 1 is that almost complete segregation of noncrystallizable species occurs during the film-forming process. This may be difficult to detect by optical methods directed to examining spherulitic morphology but would produce an increase in scattering intensity and explain the marked turbidity of the blends.

Conclusions. There is no doubt whatsoever that conventional nylon 66 is completely miscible with nylon 6I in all proportions. However, it is possible to derive an erroneous assessment of phase behavior if inappropriate preparative and analytical procedures are followed. With reference to the latter, it is concluded that when casting films of polyamide blends, TFA is an unsuitable solvent owing to the possibility of phase separation in the concentrated solution regime or segregation of the noncrystallizable component during crystallization. The latter process is of course a phenomenon of a system which is miscible in the liquid state; however, thermal analysis of a crystallized miscible mixture formed in this way may indicate a heterogeneous system. Whether or not a binary polyamide blend remains miscible during film casting will also depend upon the respective χ parameters between the polymers and the polymers and solvent.[19] This situation will of course change within a series of polyamides, such as those described by Cote and Brisson, when examined with one individual polymer such as nylon 6I. It should also be emphasized that thermal analysis of crystallized (fully or partially) polyamide blends of this nature can lead to erroneous evaluations of phase behavior.

The authors have also presented[1] a figure comparing BIM predictions with experimental data and have indicated that nylon 6,3 should be miscible with nylon 6I. Published information[7] shows this to be in error, since such a polymer would have a volume fraction of methylene groups of $x = 0.6981$. In a blend with nylon 6I, an approximate value of $\chi_{\mathrm{blend}} = 0.01$ has been estimated,[7] indicating an immiscible system. Accordingly, the criticism directed to the inability of the BIM to describe the miscibility window of nylon 6I in aliphatic polyamides is not accurate. The fact that nylon 66 is miscible with nylon 6I, taken in conjunction with the discussion above, shows that it does in fact provide an excellent description of the experimental behavior for both homopolymers and copolyamides derived from cyclic lactams. The conclusion that nylon 64 is immiscible with nylon 6I (nylon 46 was reported to be miscible with nylon 6I[7]), if a correct assessment of phase behavior, can be viewed in terms of differences in microstructure. The former contains an isolated $-(CH_2)_2-$structure adjacent to two amide groups, whereas nylon 46 contains only $-(CH_2)_4-$ units. This may be sufficient to produce distinguishing phase behavior. It is not possible to reexamine here all the blends that Cote and Brisson conclude as miscible or immiscible. The authors state that both solvent-casting, using TFA, and precipitation, using concentrated sulfuric acid, were used for preparing blends of nylon 6I with nylon *n*,*m* polymers (3,10; 4,9; 5,8; 7,6; 8,5; 9,4) and that all were immiscible. However, the authors presented no experimental evidence in support of these conclusions, and in view of the discussion above perhaps a more exhaustive analysis of these blends is required in order that unambiguous conclusions can be drawn.

In order to advance a new or alternative description of the factors that control phase behavior of binary polyamide blends, it is important that it should also incorporate all existing observations. It is evident from this discussion that the “rule of thumb” noted in the introductory comments is not applicable to these blends. Moreover, it is also clear that there is no evidence to support the hypothesis that interamide spacing is important in determining phase behavior. If the regularity of amide to amide spacing is able to explain all the published results, then perhaps a communication demonstrating how this occurs should be formulated.

References and Notes

(1) Cote, P.; Brisson, J. *Macromolecules* **1994**, *27*, 7329.
(2) Ellis, T. S. *Polymer* **1988**, *29*, 2015.
(3) Ellis, T. S. *Macromolecules* **1989**, *22*, 742.
(4) Ellis, T. S. *Macromolecules* **1990**, *23*, 1494.
(5) Ellis, T. S. *Polymer* **1990**, *31*, 1059.
(6) Ellis, T. S. *Polym. Eng. Sci.* **1990**, *30*, 998.
(7) Ellis, T. S. *Macromolecules* **1991**, *24*, 3845.
(8) Ellis, T. S. *Polymer* **1992**, *33*, 1469.
(9) Ellis, T. S. *Polym. Commun.* **1992**, *32*, 489.
(10) Ellis, T. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (2), 551.
(11) Ellis, T. S. *J. Polym. Sci., B*: *Polym. Phys.* **1993**, *31*, 1109.
(12) Ellis, T. S. *Macromolecules* **1995**, *28*, 1882.
(13) Takeda, Y.; Paul, D. R. *Polymer* **1991**, *32*, 2771.
(14) Takeda, Y.; Paul, D. R. *Polymer* **1992**, *33*, 3899.
(15) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(16) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1927.
(17) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(18) Brisson, J.; Breault, B. *Macromolecules* **1991**, *24*, 495.
(19) Robard, A.; Patterson, D.; Delmas, G. *Macromolecules* **1977**, *19*, 706.
(20) Myers, M. E.; Wims, A. M.; Ellis, T. S.; Barnes, J. *Macromolecules* **1990**, *23*, 2807.
(21) Ellis, T. S. *Polymer* **1995**, *36*, 3919.
(22) Zhikaun, C.; Ruona, S.; Karasz, F. E. *Macromolecules* **1992**, *25*, 6113.

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