

# Impact Modification of Aromatic/Aliphatic Polyamide Blends: Effects of Composition and Processing Conditions

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## SYNOPSIS

Blends of aromatic/aliphatic polyamides of varying compositions were extrusion compounded with an impact modifying reactive elastomer and injection molded. The effect of two different twin-screw blending configurations on the physical and mechanical properties of the blends was evaluated. Effects of processing conditions on blend morphology were also examined. The experimental results indicate that the extrusion sequence affects the extent of polyamide matrix-elastomer reaction as well as the morphology. The relationship between blend morphology, blend components structure and reactivity, and processing conditions with ultimate properties is discussed. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

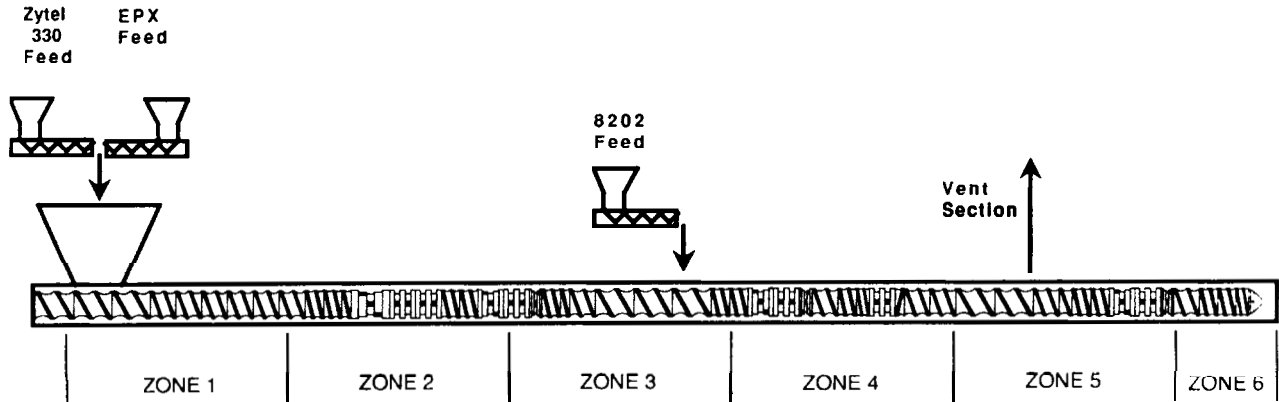
In the past it has been assumed that examples of miscible polymer blends were rather unusual exceptions to the general rule of immiscibility. However, in recent years there have been increasing numbers of literature reports detailing new miscible systems. Although most commercially viable blends are multiphase materials, in some cases miscible blends such as polyphenylene ether/polystyrene, polyvinylidene fluoride/polymethyl methacrylate and others, may offer attractive opportunities for better control over ultimate properties. With the concomitant increased understanding of how polymer molecular structure relates to blend phase behavior, scientists are better able to specifically design polymers to promote miscibility. Depending on the type of polymer, various molecular interaction mechanisms may be exploited to control the phase behavior of polymer/polymer mixtures. Work by Hu et al.<sup>1</sup> and Coleman et al.<sup>2</sup> led to the development of an automated computer program that may be used to help guide the devel-

opment of miscible blends based on such considerations. Sullivan and Weiss<sup>3</sup> reported interesting ionomer/polyamide miscible blends, whereas Dean and Harris<sup>4</sup> discussed miscible polyamide/polyester blends.

In the area of polyamide blends improved compatibility of extruded nylon 6/nylon 6,6 (N6/N6,6) blends with or without catalyst led to the presence of a single melting temperature,  $T_m$ , attributed to a random interchain copolymer formed in the melt through interchange reactions.<sup>5</sup> More recently, modification and miscibility studies of aliphatic with various rigid aromatic polyamides have been reported.<sup>6-8</sup> In a series of articles, Ellis<sup>9-11</sup> provided the foundation for understanding how subtle changes in polyamide structure govern phase behavior and led to the discovery of several miscible polyamide/polyamide blends. This work related the thermodynamics of the phase behavior to the various interactions between structural subunits of the polyamides. By controlling the ratios of aliphatic, aromatic, and amide units it is possible to move from regions of immiscibility to miscibility.

One of the miscible systems described by Ellis<sup>9</sup> is a blend of N6 (Capron® 8202) and nylon 6I-co-T (N6I-co-T, Dupont Zytel-330®). Application of

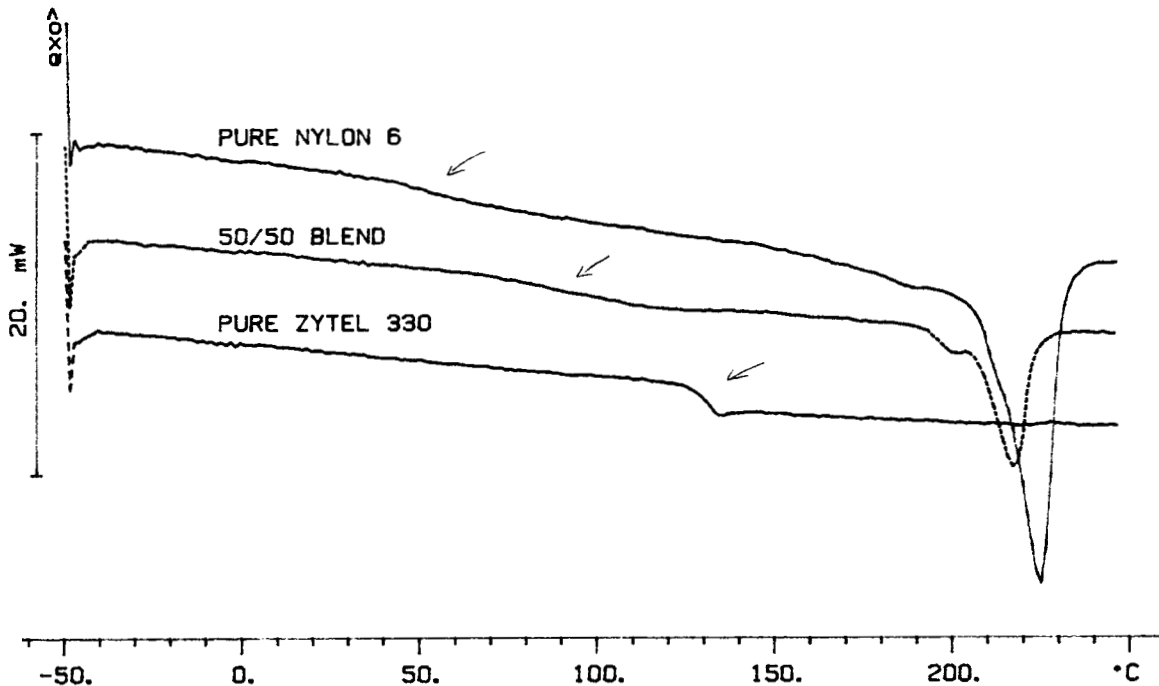
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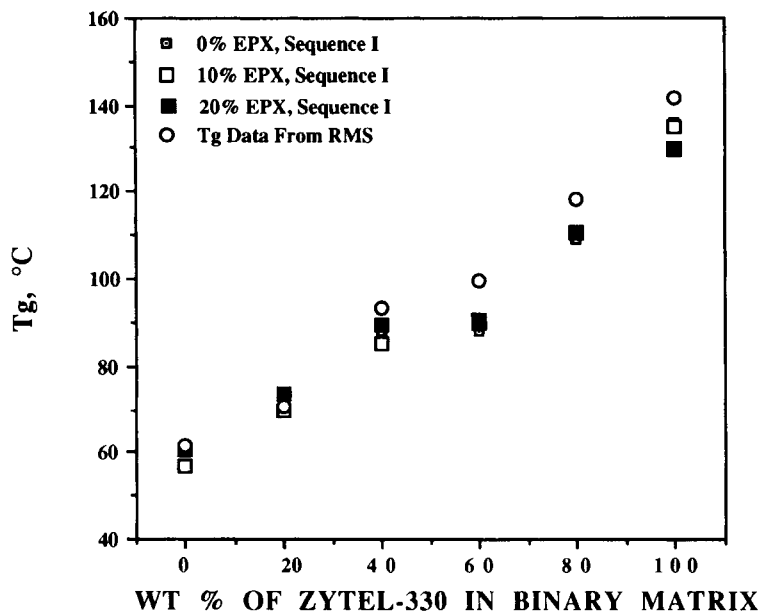
**Figure 1** Schematic process flow diagram for compounding N6 (designated as 8202), amorphous nylon (Zytel-330), and reactive elastomer (EPX). Compounding sequence II.

the repulsive interaction model<sup>9</sup> predicts a negative interaction parameter, ( $-0.014$ ), consistent with the experimentally observed phase behavior. Studies on the interaction between miscibility, crystallization behavior, and fracture toughness of N6/N6I-co-T were reported by Liu and Donovan.<sup>12,13</sup> Given the disparate properties of the two pure resins (N6 tends to be ductile and semicrystalline, whereas Zytel-330 (Z-330) is amorphous with a higher glass transition temperature,  $T_g$ , and is rather brittle), we decided to investigate the thermal and bulk mechanical properties of the

blends as a function of composition and to explore the effects of extrusion conditions and matrix composition on the properties and morphology of ternary blends containing reactive elastomeric additives (i.e., maleated ethylene-propylene rubber). Such additives, commonly used as impact modifiers in polar polymers, were first described as tougheners of various crystalline and amorphous polyamides and their blends in a series of Du Pont patents.<sup>14-16</sup> Interest in the type of system chosen in this research was also motivated by earlier work showing that subinclusions of nylon in



**Figure 2** Second-heat DSC traces for N6, Z-330, and a 50/50 blend.



**Figure 3** Comparison of  $T_g$  data of binary and ternary blends prepared according to extrusion sequence I. Squares represent DSC data on pellets. Circles represent RMS data on injection molded nylon binary blends obtained from  $\tan \delta$  vs. temperature plots.

the elastomer phase are a significant factor in the behavior of impact modified blends.<sup>17,18</sup>

## EXPERIMENTAL

The N6 was an Allied-Signal material (number average molecular weight 20,000), with a higher amine than carboxylic acid end-group concentration ( $[\text{NH}_2] : [\text{COOH}] = 3.7 : 1$ ). The Z-330 amorphous nylon based on iso/terephthalic acid and hexamethylene diamine was purchased from Du Pont and was found by potentiometric titrations to be rich in carboxy end-group functionality ( $[\text{COOH}] : [\text{NH}_2] = 4.5 : 1$ ). The maleated ethylene-propylene elastomer was Exxelor® 1803 (EPX) provided by Exxon. Prior to compounding, the nylon pellets were dried under vacuum for 6 h at 80°C or longer until moisture content was reduced to less than 0.1%.

Blends were prepared having 0, 10, and 20 wt % elastomer content with the nylon matrix resin compositions staggered at 20, 40, 60, and 80 wt %; thus, binary blends included N6/Z-330, N6/EPX, and Z-330/EPX combinations whereas ternary blends included N6/Z-330/EPX combinations. Extrusion blending was performed on a Werner & Pfleiderer 30-mm corotating twin screw extruder (model ZSK-30) equipped with ports along the barrel for side feeding and venting. Screws were configured with

conveying and mixing elements. Two different compounding sequences were used. In sequence I, applicable to both binary and ternary blends, N6, Z-330, or their pellet mixtures were fed into the extruder at the first zone; the elastomer was also fed in at the first zone (see Fig. 1) through a second feeder. In sequence II, applicable only to ternary blends, Z-330 and the elastomer were fed in at the first zone through two separate feeders; N6 was fed in separately downstream at zone 3. A vacuum was applied at zone 5. Typical process conditions were as follows: barrel temperature profile 220–265°C, melt temperatures 280–300°C, screw speed 150 rpm, feed rate approximately 7 kg/h. The second compounding sequence is illustrated schematically in Figure 1.

Extrusion compounded pellets were injection molded into ASTM test bars on a Van Dorn 75-ton press. In general, it was observed that cold molds (<30°C) were preferred in order to assist ejection and obtain uniform part quality.

Characterization of the blends and their components included: differential scanning calorimetry (DSC; Perkin-Elmer DSC-7, DSC Mettler), dynamic mechanical analysis (DMA; Rheometrics mechanical spectrometer, RMS), scanning and transmission electron microscopy (SEM and TEM), and melt flow index (MFI) at 235°C/2.16 kg (Tinius Olsen). Samples for ASTM mechanical properties were tested as is or after conditioning (annealing at

**Table I Melt Flow Index (MFI) of Components and Blends**

Z-330/N6/EPX (Sequence)	MFI, g/10 min (235°C, 2.16 kg)
100/0/0 (I)	4.4
90/0/10 (I)	1.7
80/0/20 (I)	0.35
0/100/0 (I)	24
0/90/10 (I)	0.49
0/80/20 (I)	0.52
80/20/0 (I)	7.9
72/18/10 (I)	2.8
72/18/10 (II)	2.0
64/16/20 (I)	0.39
64/16/20 (II)	0.28
60/40/0 (I)	15
54/36/10 (I)	3.2
54/36/10 (II)	2.8
48/32/20 (I)	0.29
48/32/20 (II)	0.15
40/60/0 (I)	16
36/54/10 (I)	3.5
36/54/10 (II)	3.2
32/48/20 (I)	0.19
32/48/20 (II)	0.46
20/80/0 (I)	18
18/72/10 (I)	2.3
18/72/10 (II)	4.0
16/64/20 (I)	0.25
16/64/20 (II)	0.52
0/0/100	0.82

100°C in air for 1 h followed by 50 h at room temperature and 66% relative humidity).

## RESULTS

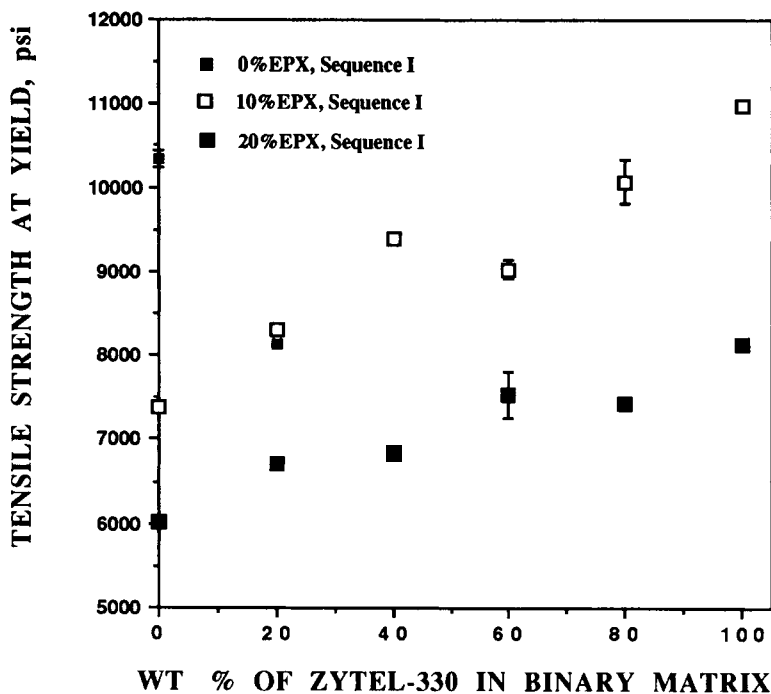
Laboratory scale studies of the Z-330/N6 binary blends confirmed Ellis' observation of miscibility.<sup>9</sup> Blends prepared via solution precipitation showed single glass transition temperatures, the accepted criterion for blend miscibility. Figure 2 shows typical DSC traces (second heating) obtained for a slowly cooled 50/50 blend and compares with the individual components. Similarly, binary blends prepared using the corotating twin screw extruder also had a single glass transition temperature.

Figure 3 shows that the  $T_g$  of the binary nylon blend increases almost linearly with increasing Z-330 content as would have been expected from property additivity rules for miscible systems. A comparison of the  $T_g$  values obtained from  $\tan \delta$  vs. temperature plots of injection molded samples

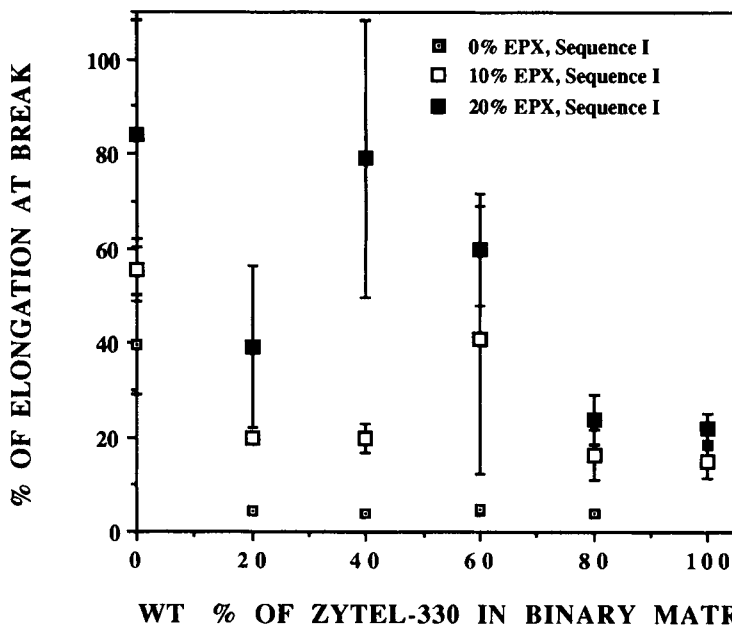
(RMS data) and DSC data on pellets (second heat scan) shows good agreement between the two methods. The presence of EPX does not seem to significantly affect the location of the blend  $T_g$ , as also shown in the DSC data of Figure 3; however, in annealing experiments with the binary and ternary blends it was shown that the  $T_g$  shifts to somewhat higher temperatures with corresponding narrower  $\tan \delta$  peaks. No significant differences in the DSC data of materials produced by the two different compounding sequences were observed. It should be noted that with the exception of the compositions with the lowest N6 content (Z-330/N6 : 80/20, Z-330/N6/EPX : 72/18/10, and Z-330/N6/EPX : 64/16/20), the presence of the melting transition with peaks around 215–230°C was always evident in the DSC scans, an indication of miscibility in the amorphous regions and possible suppression of crystallization of the N6 component when present at low concentrations.

The blend components have vastly different rheological characteristics as shown by the MFI data of Table I and are ranked in the order N6  $\gg$  Z-330 > EPX. As expected, the MFI of the binary nylon matrix varies almost linearly with composition. The addition of the more viscous EPX to either the single nylon components or their blends reduced the MFI considerably. It is of interest to note that the MFIs of all N6/EPX and Z-330/EPX blends are lower than that of the EPX alone. This could be attributed to branching/chain extension reactions that (as shown in our earlier publications<sup>19</sup>) result in significant viscosity increases and MFI reduction measurable both off-line and on-line. Also, the more rapid decrease in MFI upon the addition of EPX to N6 (from 24 to 0.5) vs. that resulting from the addition of EPX to Z-330 (from 4.4 to 1.7), suggests that the amorphous nylon is less reactive. Upon inspection of Table I, it also appears that sequence I yields somewhat higher MFIs than sequence II at compositions with high (>35%) Z-330 content.

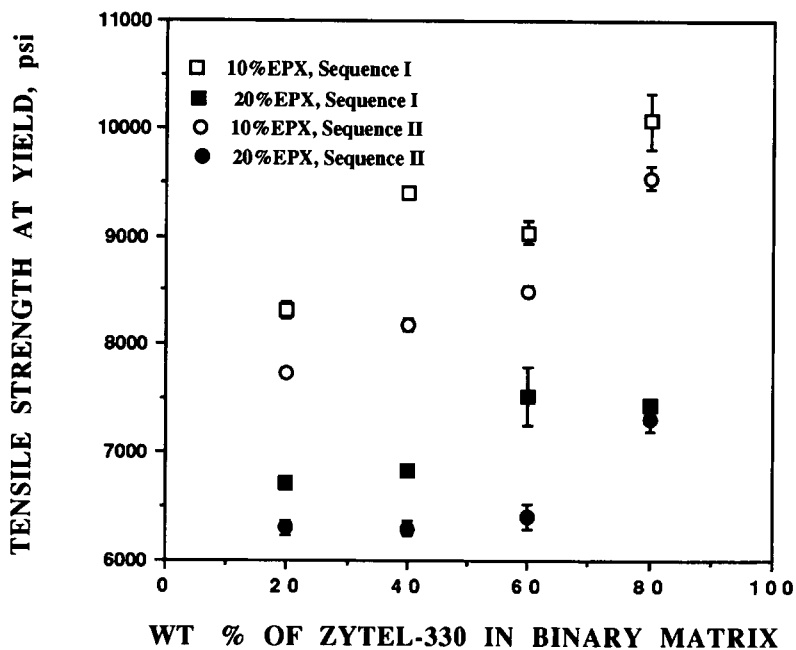
Tensile strength at yield results are shown in Figure 4 for samples processed via sequence I. The binary nylon blends and the Z-330 polymer showed brittle failure and hence no values are reported. Addition of the elastomer provided a ductile failure mode and the strength at yield values gradually increased as the concentration of Z-330 in the binary matrix was increased. For all ternary blends, elongation at yield values ranged from 5 to 7%. Total tensile strain at break values showed considerable scatter but were uniformly higher as the elastomer content was increased (Fig. 5); more dramatic increases (up to 80% elongation at break) were ob-



**Figure 4** Tensile strength at yield vs. composition of binary and ternary injection molded samples prepared according to extrusion sequence I. Samples were annealed and conditioned prior to testing (psi  $\times$  6.895 = kPa). Zytel-330 and binary matrix blends containing it do not show any yield.



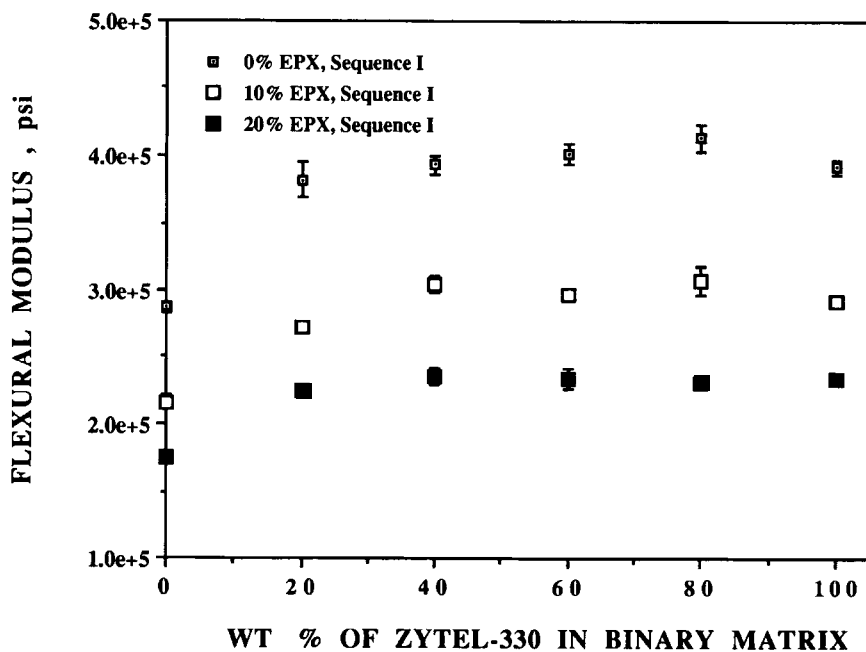
**Figure 5** Elongation at break vs. composition of binary and ternary injection molded samples prepared according to extrusion sequence I. Samples were annealed and conditioned prior to testing.



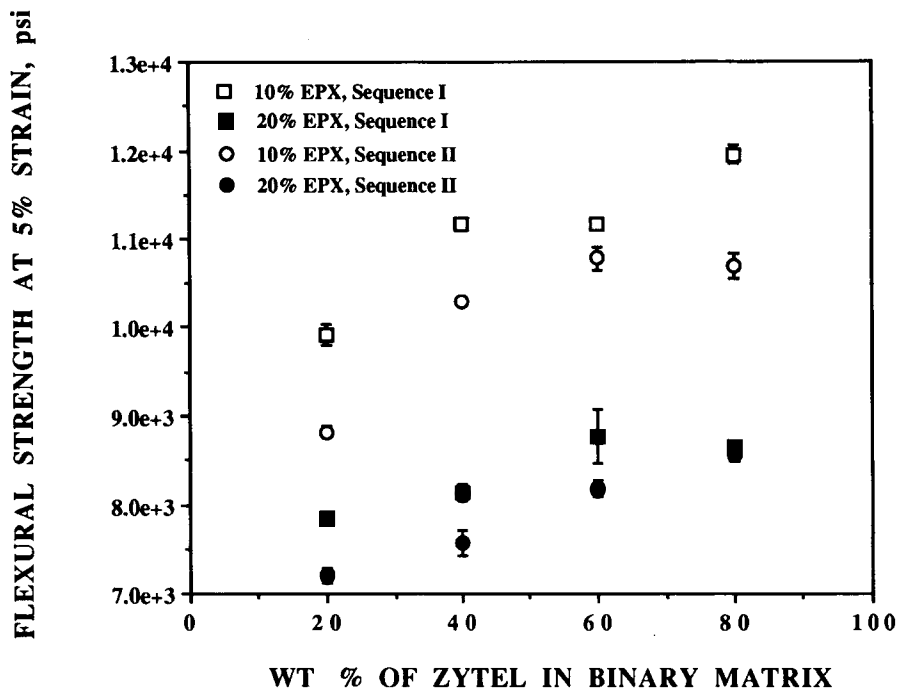
**Figure 6** Comparison of tensile yield strength vs. composition of ternary injection molded samples prepared according to extrusion sequences I and II. Samples were annealed and conditioned prior to testing (psi  $\times$  6.895 = kPa).

served for blends containing 40–60% Z-330 in the binary matrix. Changing the extrusion process conditions to sequence II resulted in uniformly lower tensile strength at yield values (see Fig. 6).

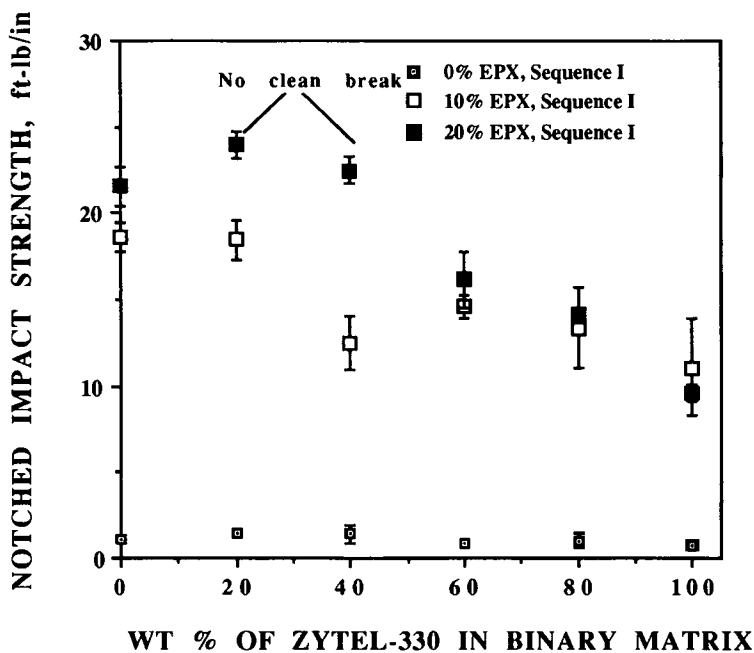
Flexural modulus values, as shown in Figure 7, are increased with the addition of the amorphous nylon but remain level at contents above 20 wt % when the blends are processed according to sequence I.



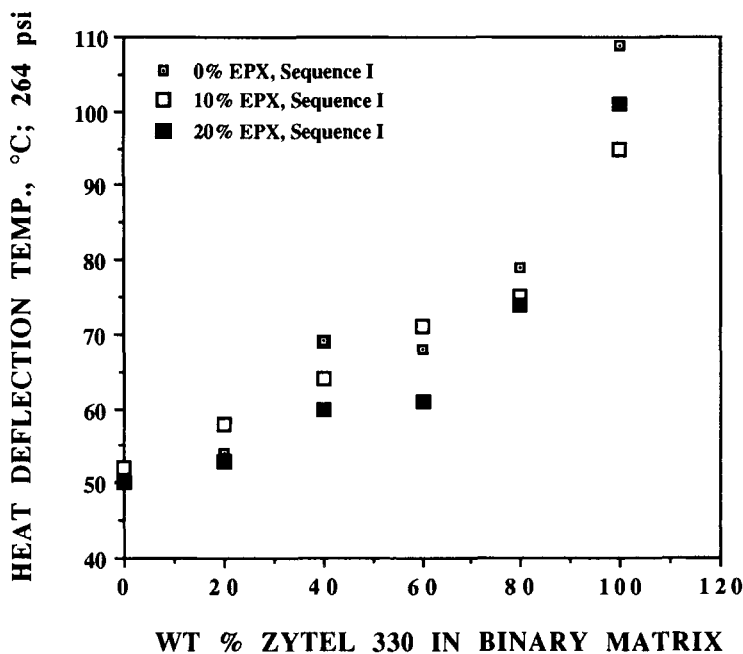
**Figure 7** Flexural modulus vs. composition of binary and ternary injection molded samples prepared according to extrusion sequence I. Samples were annealed and conditioned prior to testing (psi  $\times$  6.895 = kPa).



**Figure 8** Comparison of flexural strength vs. composition of ternary injection molded samples prepared according to extrusion sequences I and II. Samples were annealed and conditioned prior to testing (psi  $\times$  6.895 = kPa).



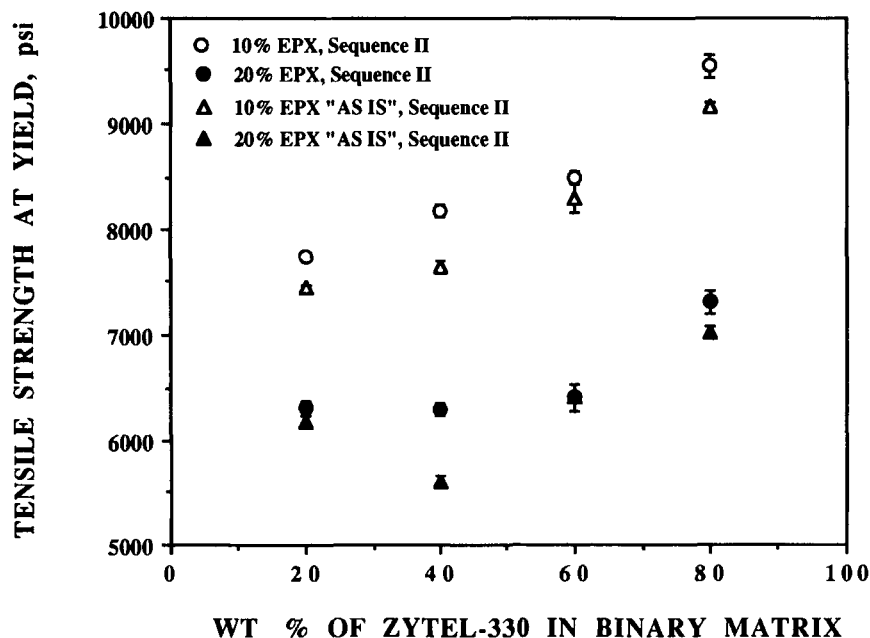
**Figure 9** Notched Izod impact strength vs. composition of binary and ternary injection molded samples prepared according to extrusion sequence I. Samples were annealed and conditioned prior to testing (ft-lb/in  $\times$  5.338 = J/m).



**Figure 10** Heat deflection temperature vs. composition of binary and ternary injection molded samples prepared according to extrusion sequence I. Samples were annealed and conditioned prior to testing ( $\text{psi} \times 6.895 = \text{kPa}$ ).

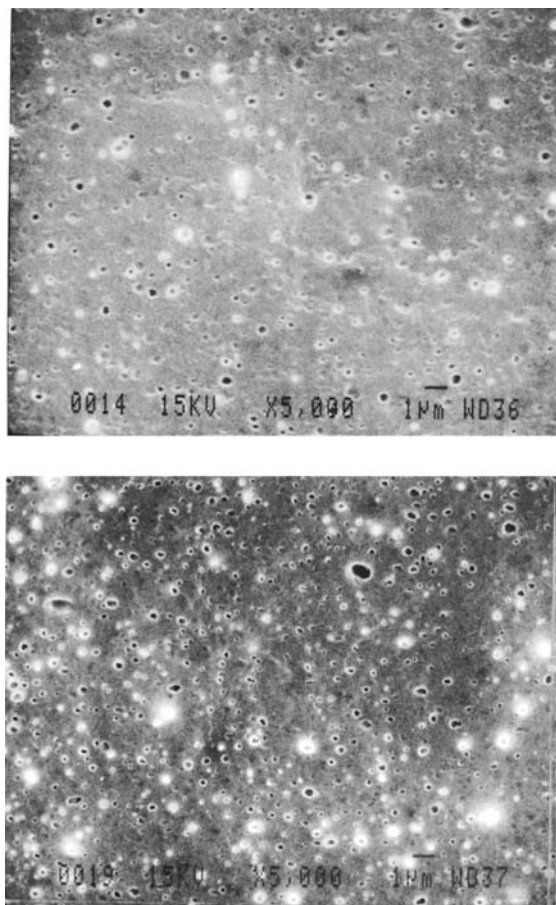
As expected, incorporation of the EPX lowers flexural modulus proportionately. A more continuous, although modest, gradual increase in flexural strength is observed as the amorphous nylon con-

tent is increased. Again, the extrusion process sequence II reduces the overall flexural property values as exemplified by the strength data shown in Figure 8.



**Figure 11** Comparison of tensile yield strength vs. composition of sequence II ternary blends that were either annealed/conditioned or tested as is after injection molding ( $\text{psi} \times 6.895 = \text{kPa}$ ).





**Figure 12** SEM microphotographs of extruded sequence I (upper) and sequence II (lower) ternary blends Z-330/N6/EPX : 36/54/10 after EPX extraction. Original magnification  $\times 5000$ .

Notched Izod impact testing of these materials as a function of process conditions and composition was also undertaken. For pure N6, addition of 10% of the elastomer increases the impact resistance significantly (see Fig. 9). A further increase is noted as the level of elastomer incorporation is increased to 20%. Likewise, the pure amorphous nylon benefits from addition of the elastomer, although ultimate toughness values do not reach those observed for the pure N6. In the case of the blends, there appears to be a mild synergistic effect as evidenced by a maximum in impact properties for samples containing 20–40% Z-330 in the nylon matrix. This occurs for blends containing 20% of the impact modifier. In general, the impact properties were poorer for the blends processed using the second extrusion sequence. Heat deflection temperature (HDT) vs. composition curves are shown in Figure 10. Similarly to the previously presented  $T_g$  trends, HDT in-

creases with increasing Z-330 content. However, the presence of the elastomer results in some modest HDT decreases.

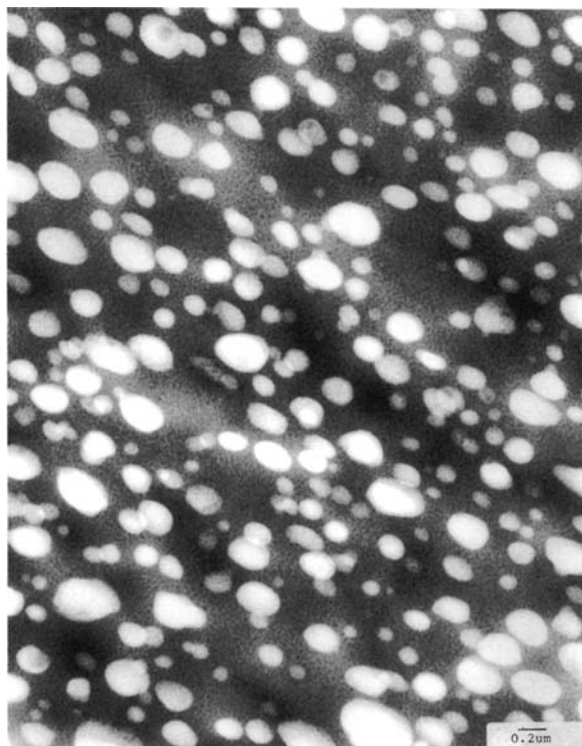
## DISCUSSION

As evidenced by the single  $T_g$  observed by DSC and confirmed by DMA measurements, the amorphous region of N6 appears to be miscible with the 100% amorphous Z-330 nylon when processed using conventional twin-screw extrusion techniques. Because it is well known that the manner in which a blend is prepared can affect the phase behavior, it is of interest to note that earlier experiments conducted on blends prepared via either solvent precipitation or using a single screw extruder also showed the system to be miscible. Addition of the elastomer did not alter the level of miscibility on the dimensional scale of the DSC thermal analysis technique. However, if we were to probe the samples on a smaller dimensional scale via techniques such as NMR, we might be able to observe some differences.

One interesting observation for both extrusion prepared blends and solution precipitated samples was the inflection in the  $T_g$  versus composition be-



**Figure 13** TEM microphotograph of injection molded sequence I ternary blend Z-330/N6/EPX : 16/64/20.



**Figure 14** TEM microphotograph of injection molded sequence I ternary blend Z-330/N6/EPX : 78/18/10.

havior at about 50% Z-330 content (see Fig. 3). We attribute this to the fact that blends rich in N6 are partially crystalline. The crystallization of the N6 is in effect a phase separation process that serves to enrich the amorphous nylon fraction of the non-crystalline regions in the blends. This raises the  $T_g$  somewhat above the values expected, based on the rule of mixtures weight fraction composition for the N6-rich blends.

During molding of the samples, it was observed that both binary and ternary blends containing more than 30% Z-330 required cold mold conditions. Typical mold temperatures for pure N6 averaged 50–70°C. Higher mold temperatures for the blends resulted in difficulties ejecting parts and poor part quality, unless very long hold times were used. We measured the temperatures at which onset of N6 crystallization occurred as a function of blend composition and found that the addition of the amorphous nylon impedes N6 crystallization significantly. During the molding process the lower mold temperatures served to quench cool the test bars. Even blends rich in N6 (60–70%) were observed to be rather transparent when processed under these conditions and required a cold mold. Subsequent annealing of the test bars increased the crystalline

fraction of the N6 component as measured by DSC and X-ray scattering methods. This annealing step results in a slight improvement in properties, as exemplified by the tensile strength data of Figure 11.

Addition of the maleated ethylene-propylene elastomer improved the impact properties significantly, as expected. In the case of pure N6, values approaching those of commercial “supertough” formulations were observed. Other investigators observed that blends of pure N6 with maleated styrene/butadiene copolymers are not supertough, due to elastomer particle sizes smaller than a critical lower limit of 0.3  $\mu\text{m}$ .<sup>20,21</sup> It was proposed that this is due to the monoamine end-group functionality of the N6 used in their study, which leads to formation of graft copolymer species with the maleated elastomer that are more efficient in reducing particle size. In our case we utilized a N6 variant having an enriched (70%) amine end-group content. Our observation of normal elastomer particle sizes (from approx. 0.3 to 1.0  $\mu\text{m}$ ) is consistent with the results obtained by other researchers.<sup>22</sup> However, we did observe poorer properties for materials prepared via process sequence II, in which the N6 was fed into to the extruder downstream following the premixed Z-330/elastomer fraction. This is consistent with a shorter residence time and, hence, less reaction with the diamine terminated N6. In fact, comparison of the N6 rich blends (Z-330/N6/EPX : 36/54/10) in Figure 12 seems to indicate that there is more rubber extraction (2 h in boiling xylene) for the sequence II sample than for the sample of sequence I; this could also imply less reaction.

TEM analysis of injection molded samples indicated complex morphologies, often with elongated particles and phase inversion depending on composition. Although most samples contained fairly regular inclusions with little clustering and no sub-inclusions, some samples were more complex; for example, Z-330/N6/EPX : 16/64/20 samples contained many irregularly shaped elastomer particles with irregular inclusions (Fig. 13). The morphology of the nylon matrix was also of interest: separation of the Z-330 and N6 into a blocklike morphology appeared to occur when the Z-330/N6 ratio was  $>1$  (Fig. 14), although such behavior was not evident when the Z-330/N6 ratio was  $<1$ .

## CONCLUSIONS

Conventional twin-screw extrusion followed by injection molding of amorphous Z-330 polyamide and N6 results in blends containing a miscible amor-

phous phase and a crystalline N6 phase, consistent with laboratory-scale solvent based preparative methods. Addition of a reactive maleated elastomer results in supertough impact properties with a modest decrease in heat-distortion temperature that is partially offset by the incorporation of the higher  $T_g$  amorphous polyamide. Observations as to rubber particle sizes, extrusion blending sequence, and impact behavior are consistent with other work relating to the reactivity of the matrix polymer end groups with the rubber phase.

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