

# Modification of Nylon-6 with Wholly Rigid Poly(*m*-phenylene isophthalamide)

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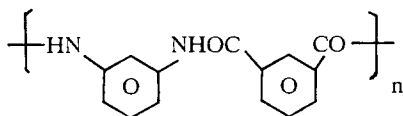
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## SYNOPSIS

In this study, the flexible nylon-6 was reinforced by the wholly rigid aromatic polyamide poly(*m*-phenylene isophthalamide) (PmIA) (Nomex) by physical polyblending and chemical copolymerization using *p*-aminophenylacetic acid (P-APA) as a coupling agent. From DSC measurements, it was shown that  $T_g$  of the polyblends increased with the increase of Nomex content. The  $T_g$  and  $T_m$  of multiblock copolyamides were found to be higher than those of polyblends and triblock copolyamides. Scanning electron microscopy revealed that the polyblends were a dispersed phase structure, although the multiblock copolyamides exhibited a homogeneous texture rather than an aggregated one. From the wide-angle X-ray diffraction pattern, it was found that the triblock copolyamides and polyblends had two diffraction peaks, i.e.,  $2\Theta = 20.5$  and  $24^\circ$ . However, the multiblock had only one at  $2\Theta = 20^\circ$ , indicating a different crystal structure for multiblock copolyamides. For the mechanical properties, it was found that the multiblock copolyamides had a more significant reinforcing effect than those of polyblends and triblock copolyamides.

## INTRODUCTION

Recently, a number of attempts were made to increase the mechanical properties of the aliphatic nylons by using physical blending and chemical modification with aromatic polyamides such as Kevlar, polybenzamide (PBA),<sup>1-4</sup> or poly(4,4'-diphenylsulfone terephthalamide) (PSA).<sup>5,6</sup> As shown in our previous papers,<sup>5,6</sup> the aliphatic nylon-6 when modified by the semi-rigid PSA exhibited better thermal and mechanical properties. For this study, we used wholly rigid polyamide poly(*m*-phenylene isophthalamide) (PmIA) to reinforce the aliphatic nylon-6. The chemical structure of PmIA (Nomex) is as follows:



The wholly rigid Nomex has a triclinic crystal structure<sup>7,8</sup> unlike the monoclinic crystal structure<sup>9-11</sup> of nylon-6. The different crystal structures

could affect the crystallization pattern of polyblends and copolymers.

## EXPERIMENTAL

### Materials

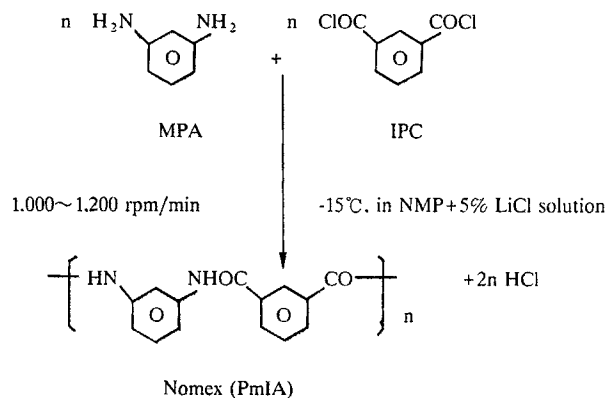
The nylon-6 was obtained from the Formosa Chemical and Fiber Corporation. The sample was first dissolved in formic acid and then poured into a large amount of water. Samples were refluxed with methanol and hot water for 16 h and after that dried at  $100^\circ\text{C}$  under vacuum for 8 h. Its inherent viscosity ( $\eta_{inh} = 1.24$ ) and  $\bar{M}_n$  (21,500) were obtained according to the literature.<sup>12</sup>

Isophthaloyl dichloride (IPC), *m*-phenylene diamine (MPA), and *p*-aminophenyl acetic acid (P-APA) were purchased from Merck Co., and used as received.

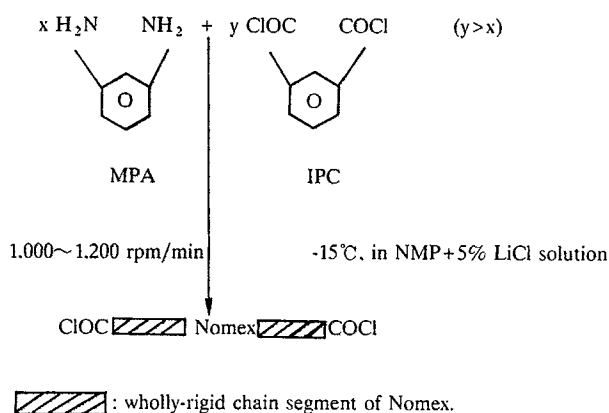
*N*-methyl-2-pyrrolidone (NMP) was first distilled over  $\text{CaH}_2$  at  $92-94^\circ\text{C}/14$  mm Hg and then stored in the molecular sieves. The moisture content of a 5% LiCl solution in NMP was 0.018 wt % by the Karl-Fischer Moisture Meter, MKA-3, Kyoto Electronic. Lithium chloride (LiCl) was dried under vacuum at  $160^\circ\text{C}$  for 5 h.

### Preparation of Polyamides and Their Prepolymers

High molecular weight wholly rigid Nomex (PmIA) was polymerized by low-temperature solution polymerization in NMP containing 5% LiCl at  $-15^{\circ}\text{C}$  for 30 min.<sup>5,8</sup> The reaction scheme is as follows:

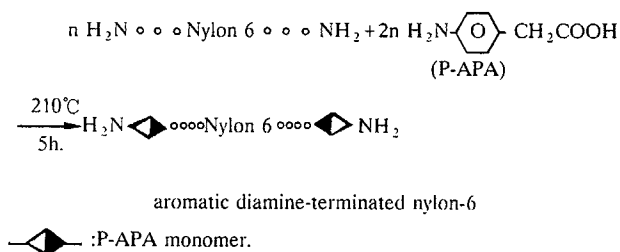


Similarly, the low molecular weight Nomex was also prepared by excess IPC with MPA in NMP + 5% LiCl solution, i.e.,

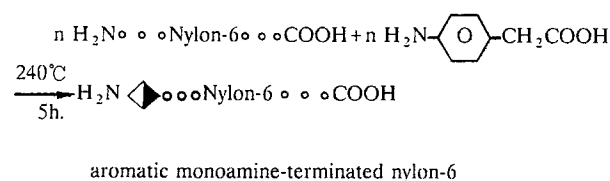


A low molecular weight diamine-terminated nylon-6 prepolymer was prepared by an excess of hexamethylene diamine (HMDA) as described in the literature.<sup>13,14</sup> The prepolymer was reacted with P-APA coupling agent at  $210^{\circ}\text{C}$  for 5 h. The product

was purified and dissolved in a NMP + 5% LiCl solution for further use.



The long chain monoamine-terminated nylon-6 prepolymer was also prepared by bulk polymerization at  $240^{\circ}\text{C}$  for 5 h. The reaction scheme is shown as follows:



Number average molecular weights are given in Table I. The  $\bar{M}_n$  and  $\bar{M}_w/\bar{M}_n$  were determined by Waters Gel Permeation Chromatograph. Solvent was *N,N*-dimethylformamide containing 0.05 mol/L LiCl. The column was  $\mu$ -BONDAGEL E-Linear, which was calibrated at a flow rate of 1 mL/min.

### Synthesis of Nylon-6-Nomex Block Copolymers

The copolyamides were synthesized by reacting nylon-6 prepolymer with the Nomex prepolymer using the following procedure. The aromatic diamine-terminated nylon-6 prepolymer ( $\bar{M}_n = 1,300$ ) or monoamine-terminated nylon-6 prepolymer ( $\bar{M}_n = 10,700$ ) in NMP + 5% LiCl (A bath) and the aramid Nomex prepolymer ( $\bar{M}_n = 820$ ) also in NMP + 5% LiCl (B bath) were allowed to mix and stirred vigorously in  $\text{N}_2$  atmosphere system at  $-5$ – $-10^{\circ}\text{C}$  for 30 min, then raised to room temperature, and stirred continuously for 1 h. Finally, a homogeneous

**Table I** Characteristics of Prepolyamides and PmIA

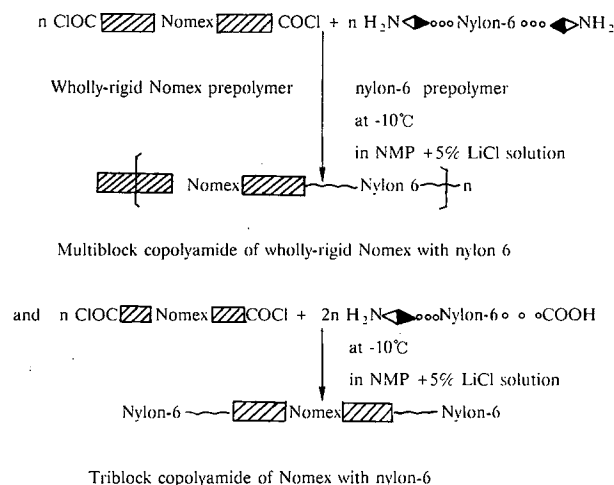
| Polymer <sup>a</sup> | N6<br>Prepolymer | N6 <sub>a</sub><br>Prepolymer | PmIA<br>Prepolymer | PmIA                            |
|----------------------|------------------|-------------------------------|--------------------|---------------------------------|
| $\bar{M}_n^b$        | 998              | 1,300                         | 826                | $1.46 \times 10^5$ <sup>c</sup> |

<sup>a</sup> N6, amine-terminated nylon-6 prepolymer (by HMDA); N6<sub>a</sub>, aromatic diamine-terminated nylon-6 prepolymer (by P-APA). Elemental analysis (%): C, (64.2); H, (9.6); N, (12.5).

<sup>b</sup>  $\bar{M}_n = 15.600 \times \eta_{inh}^{1.49}$  according to the literature.<sup>8</sup>

<sup>c</sup> From GPC measurement.

viscous solution was obtained and poured into an aqueous solution containing equivalent LiOH. The precipitate was filtered and dried at 80°C under vacuum for 7 h. All the copolyamides obtained here were soluble in the NMP + 5% LiCl solution, but they were not soluble in formic acid or *m*-cresol, which were good solvents for nylon-6. The detailed reaction schemes are as follows:



The various multiblock and triblock copolyamides were prepared by low-temperature polymerization of nylon-6 prepolymer with different amounts (wt %) of wholly rigid Nomex prepolymers. The inherent viscosities of the block copolyamides were found to be greater than those of the prepolymers, suggesting that the block copolyamides were higher molecular weight. In general, the chain extending reaction could be completed in 10–15 min and yielded as high a molecular weight copolymer as those of nylon-6-PSA copolyamides in our previous paper.<sup>5,6</sup> All nylon-6-Nomex copolyamides are summarized in Table II.

### Blends of Aramid Nomex and Nylon-6

In this study, the high molecular weight nylon-6 ( $\bar{M}_n = 21,500$ ) was blended physically with various ratios (1, 3, 5, 10, 15, and 20%) of high molecular weight wholly rigid Nomex (PmIA) as described by Takayanagi et al.<sup>1,2</sup> The mixtures were dissolved in 98% H<sub>2</sub>SO<sub>4</sub>. The clear, single-phase solutions were casted on a glass plate, and then placed into slowly flowing water to precipitate the blends. The precipitated blends were washed until free of acid, and dried under vacuum at 80°C. Films were molded by hot pressing at 240°C and cooled at a cooling rate of about 15–20°C/min to room temperature, and finally annealed at 210°C for 1 h in nitrogen atmosphere.

**Table II Characteristics of Block Copolyamides**

| Code <sup>a</sup> | Polymer                                | Nomex (wt %) | Reaction Time (h) | $\eta_{inh}^b$ |
|-------------------|--|--------------|-------------------|----------------|
| B <sub>M1</sub>   | N6-b1-Nomex                            | 10           | 0.5               | 1.26           |
| B <sub>M2</sub>   | N6-b2-Nomex                            | 15           | 0.5               | 1.39           |
| B <sub>M3</sub>   | N6-b3-Nomex                            | 20           | 0.5               | 1.58           |
| B <sub>T1</sub>   | N6 <sub>a</sub> -Nomex-N6 <sub>a</sub> | 10           | 0.5               | 1.35           |
| B <sub>T2</sub>   | N6 <sub>a</sub> -Nomex-N6 <sub>a</sub> | 15           | 0.5               | 1.48           |
| B <sub>T3</sub>   | N6 <sub>a</sub> -Nomex-N6 <sub>a</sub> | 20           | 0.5               | 1.59           |
| N6                | Nylon-6 prepolymer                     | 0            | —                 | 0.11           |
| N6 <sub>a</sub>   | Long-chain nylon-6                     | 0            | —                 | 0.78           |

<sup>a</sup> B<sub>M1</sub>–B<sub>M3</sub>, multiblock copolymer; B<sub>T1</sub>–B<sub>T3</sub>, triblock copolymer by the use of P-APA coupling agent. N6, amine-terminated nylon-6 prepolymer ( $\bar{M}_n = 1000$ ); N6<sub>a</sub>, aromatic monoamine-terminated nylon-6 prepolymer ( $\bar{M}_n = 10,700$ , measured in *m*-cresol at 25°C).<sup>8</sup>

<sup>b</sup> Measured at a concentration of 0.5 g dL<sup>-1</sup> in NMP + 5% LiCl at 30°C.

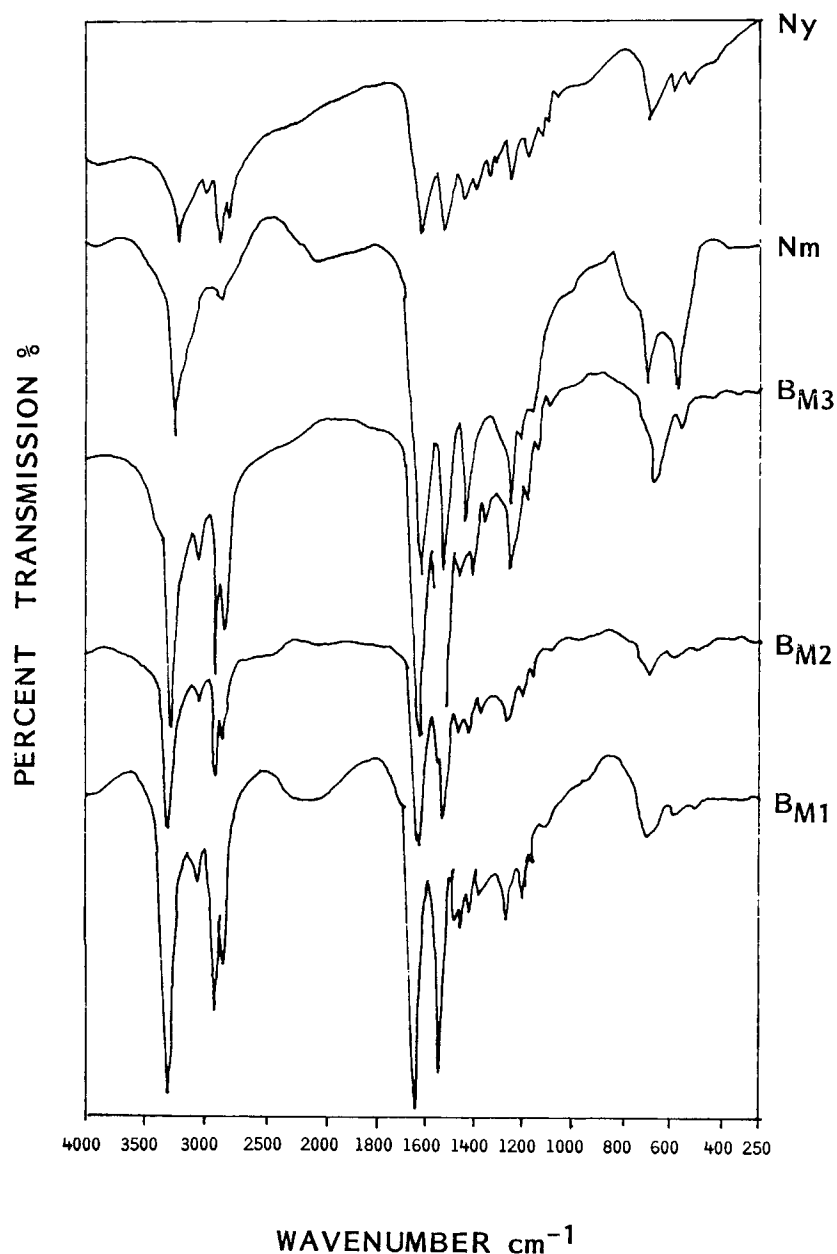
### Measurements

Infrared spectra of homopolymers and copolymers were obtained by Hitachi Model 260-50 Type, over a range 400–4,000 cm<sup>-1</sup>. The samples were in the form of film about 10 μm thickness. Elemental analysis (C.H.N.) was performed by Heraeus CHN-O-Rapid Analyzer. Differential scanning calorimetry (DSC) was used to measure the temperature of crystallization ( $T_c$ ) and the degree of crystallinity ( $X_c$ ) in nitrogen atmosphere with a Du Pont model 9900 DSC, at a heating rate of 20°C/min to obtain the glass temperature ( $T_g$ ) and the melting temperature ( $T_m$ ). Wide-angle X-ray photographs were taken with Ni-filter CuK α radiation using RigaKu D/max-II Type X-ray Diffractometer. A scanning electron microscope, Cambridge Stereoscan-600, was also used to observe the morphological structure on samples that were sputter-coated with Au to prevent their oxidation. All stress-strain datas were obtained on the Instron 1122 Type testing instrument at an extension rate of 5 mm/min, and the full load was 50 kg.

## RESULTS AND DISCUSSION

### Analysis of Infrared Spectra

Infrared spectra were obtained by using the thin film technique. The transmission IR spectra of homopolymers and block copolymers are shown in Figure 1, respectively. The IR spectra of nylon-6 (curve 1, respectively. The IR spectra of nylon-6 (curve N<sub>y</sub>) were characterized at 3,300 cm<sup>-1</sup> (=N–H



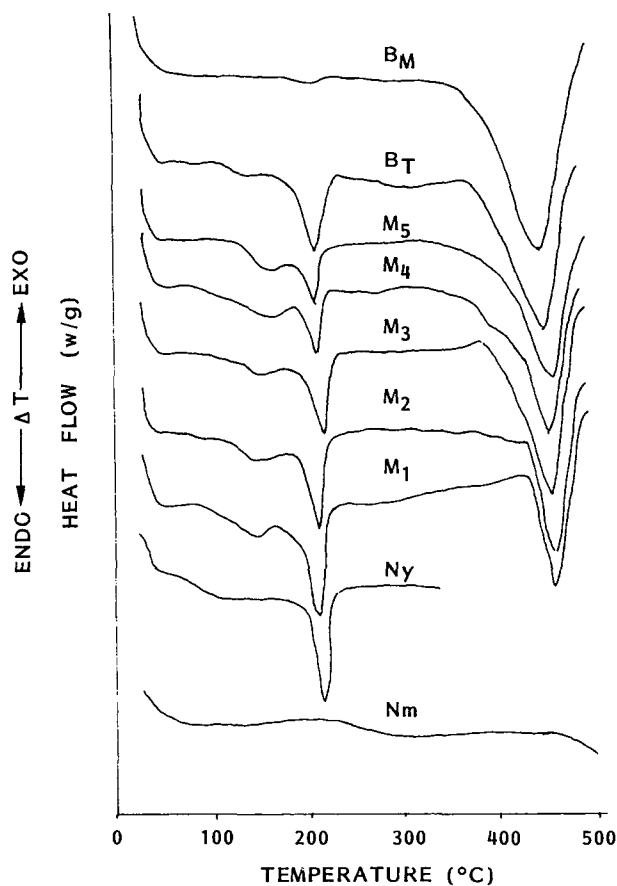
**Figure 1** Infrared spectra of homo- and copolyamide films: ( $N_y$ ), nylon-6 homopolymer; ( $N_m$ ), Nomex homopolymer; ( $B_{M1}$ – $B_{M3}$ ), multiblock copolyamides of Nomex 10, 15, and 20%.

stretch vibration),  $1,650\text{ cm}^{-1}$  ( $=\text{C}-\text{O}$ ),  $1,560\text{ cm}^{-1}$  ( $=\text{N}-\text{H}$  deformation), and  $2,900$  and  $2,770\text{ cm}^{-1}$  ( $-\text{CH}_2-$  stretch vibration) absorptions. The characteristic IR spectra of Nomex (curve  $N_m$ ) were shown at  $3,400\text{ cm}^{-1}$  ( $\text{N}-\text{H}$  stretch vibration),  $1,680\text{ cm}^{-1}$  ( $=\text{C}-\text{O}$ ),  $1,610\text{ cm}^{-1}$  and  $1,540\text{ cm}^{-1}$  ( $\text{C}-\text{C}$ ),  $1,315$ – $1,550\text{ cm}^{-1}$  ( $=\text{N}-\text{H}$  on metasubstituted), and  $3,000$ – $3,150\text{ cm}^{-1}$  ( $=\text{N}-\text{H}$  on parasubstituted) absorptions. The nylon-6–Nomex block copolymers

(curve  $B_{M1}$ – $B_{M3}$ ) did show both the characteristic absorption of nylon-6 and Nomex. Noticeable was a characteristic absorption of the  $-\text{CONH}-$  at  $1,315$ – $1,550\text{ cm}^{-1}$  on metasubstituted and at  $3,000$ – $3,150\text{ cm}^{-1}$  for parasubstituted for the block copolymers with P-APA as a coupling agent. This came from the reaction of the  $-\text{NH}_2$  on paraposition of benzene with the metaposition  $-\text{COCl}$  group of Nomex prepolymer.

### Thermal Properties of Block Copolymers and Polymer Blends

Polymers with aromatic ring structure could contribute to their thermal stability. In this study, the presence of aromatic Nomex in nylon-6 could be expected to provide better thermal properties. The thermal behavior of homopolymers, polyblends, and block copolymers that were measured by DSC are shown in Figure 2 and Table III. The results show that the transition temperature ( $T_g$ ) of the polyblends of nylon-6/Nomex was increased with the increase of Nomex wt % content. This indicates that the micro-Brownian motion of amorphous nylon-6 chains did suffer from the restraint of the wholly rigid Nomex molecules, especially if the amounts of Nomex were increased. Surprisingly, it was found that the  $T_m$  of polyblends did not change much. It



**Figure 2** DSC plots of polyblends of nylon-6 with Nomex and nylon-6-Nomex block copolymers in nitrogen: ( $N_m$ ), Nomex; ( $N_y$ ), nylon-6; ( $M_1$ ), Nomex 1%; ( $M_2$ ), Nomex 5%; ( $M_3$ ), Nomex 10%; ( $M_4$ ), Nomex 15%; ( $M_5$ ), Nomex 20%; ( $B_T$ ), triblock copolyamide of 15 wt % Nomex content; ( $B_M$ ), multiblock copolyamide of 15 wt % Nomex content.

**Table III**  $T_g$ ,  $T_m$ , and Crystalline Properties Measured by DSC Analysis

| Code  | Polymer   | $T_g$<br>(°C) | $T_m$<br>(°C) | $X_c$<br>(%) | $\Delta H_{fus}$<br>(J/g) |
|-------|-----------|---------------|---------------|--------------|---------------------------|
| $N_y$ | Nylon-6   | 67            | 219           | 24           | 43                        |
| $N_m$ | Nomex     | 275           | 473           | —            | —                         |
| $M_1$ | Nomex 1%  | 127           | 217           | 31           | 57.9                      |
| $M_2$ | Nomex 5%  | 130           | 218           | 38           | 71.8                      |
| $M_3$ | Nomex 10% | 134           | 223           | 43           | 80.6                      |
| $M_4$ | Nomex 15% | 139           | 216           | 40           | 75.5                      |
| $M_5$ | Nomex 20% | 140           | 218           | 39           | 73.7                      |
| $B_T$ | Nomex 20% | 112           | 198           | —            | —                         |
| $B_M$ | Nomex 20% | 140           | 454           | —            | —                         |

$B_T$ , triblock copolyamide (Nomex content of 20 wt %);  $B_M$ , multiblock copolyamide (Nomex content of 20 wt %);  $M_1$ – $M_5$ , polyblends of nylon-6 with Nomex.

still remained at about 219°C for the nylon-6/Nomex series ( $M_1$ – $M_6$ ). This result was also seen in our previous work for nylon-6/PSA polyblends.<sup>5,6</sup> It also indicates that the Nomex molecules dispersed among the nylon-6 matrix could act as “nucleating agents” and accelerate the growth rate of nylon-6 crystallization. This phenomenon is consistent with the PPTA/nylon-6 and PBA/nylon-6 molecular composites as described by Takayanagi et al.<sup>1</sup> It is also consistent with our previous work for PSA/nylon-6 polyblends,<sup>5,6</sup> and is demonstrated by the increase of degree of crystallinity ( $X_c$ ) as shown in Table III. The values of degree of crystallinity were calculated from eq. (1)

$$X_c = \frac{\Delta H_s}{\Delta H_f} \times 100\%, \quad (1)$$

where  $X_c$  is the degree of crystallinity for specimens,  $\Delta H_s$  (J/g) is the heat capacity for specimens under investigation, and  $\Delta H_f$  is the heat fusion for 100% crystalline nylon-6, which was 189 J/g.<sup>15,16</sup> From Table III, it was shown that the degree of crystallinity increased as the proportion of Nomex was increased. However, the polymer blend with 15 wt % of Nomex exhibited a decrease of crystallinity. This suggests that the addition of excess amounts of Nomex could result in a decrease of the thermal mobility of nylon-6 due to the restraint of the immobile and wholly rigid Nomex segments.

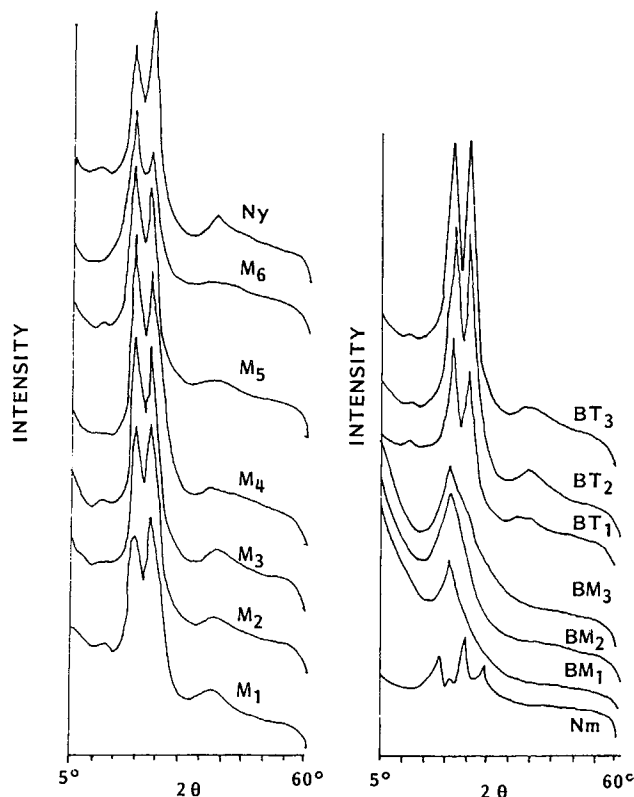
It is also shown in Figure 2 and Table III that the glass transition temperature ( $T_g$ ) and the melting point ( $T_m$ ) of the block copolyamides increased significantly as compared with that of the original

nylon-6, and were also higher than those of the blends. Since the transition temperature could indicate the behavior of molecular motion within the polymer, it could be used as a clue to identify the phase separation, or their compatibility.<sup>12</sup> The glass transition temperature ( $T_g$ ) of multiblock copolyamides showed only one peak; therefore, a compatible state of wholly rigid Nomex with nylon-6 could be possible in the multiblock copolymer. From DSC analysis, it is seen that the melting temperature of the multiblock copolyamides was up to 400°C. Noticeably, the homopolymer of PmIA (Nomex) having triclinic structure<sup>7,8</sup> isn't the same as that of monoclinic structure nylon-6.<sup>9-11</sup> Its block copolyamides also exhibited higher  $T_g$  and  $T_m$  because the nylon-6-Nomex multiblock copolyamide had formed a new crystal structure.

### Wide-Angle X-ray Diffraction

The wide-angle X-ray diffraction patterns of nylon-6 homopolymers, polyblends, and block copolymers were measured by the Rigaku diffractometer. From the result of X-ray diffractions (Table IV) on the blends of nylon-6 with wholly rigid Nomex, the crystallite size of nylon-6 apparently became smaller as the amount of Nomex was increased.

Data show an increase in crystallinity and a reduction in crystallite size of the nylon-6 matrix in Table IV. However, it should be noted that the crystallite size in the  $\alpha$  (002,202) plane became smaller, but that in the  $\alpha$  (200) plane it did not, as wholly rigid Nomex was present. In addition, the d-spacing remained at almost a constant value. Thus, it could be concluded that if more content of the aromatic polyamide was blended, the more the crystal growth



**Figure 3** X-ray diagrams of homopolymers, polyblends, and block copolyamides: ( $N_y$ ), nylon-6 100%; ( $N_m$ ), Nomex 100%; ( $M_1$ ), Nomex 1 wt %; ( $M_2$ ), Nomex 3 wt %; ( $M_3$ ), Nomex 5 wt %; ( $M_4$ ), Nomex 10 wt %; ( $M_5$ ), Nomex 15 wt %; ( $M_6$ ), Nomex 20 wt %; ( $B_{T1}$ ,  $B_{T2}$ ,  $B_{T3}$ ), triblock copolyamides of 10, 15, and 20 wt % Nomex content; ( $B_{M1}$ ,  $B_{M2}$ ,  $B_{M3}$ ), multiblock copolyamides of 10, 15, and 20 wt % Nomex content.

of nylon-6 chain in the  $\alpha$  (002,202) plane could be retarded. The effect of wholly rigid chain Nomex was greater than that of semi-rigid chain poly(4,4'-

**Table IV** D-spacing, Crystallite size, and Degree of Crystalline of Nylon-6-Nomex Polyblends and Block Copolyamides

| Code <sup>a</sup> | Polymer        | $\text{\AA}$<br>d(200) | $\text{\AA}$<br>d(002, 202) | $\text{\AA}$<br>L(200) | $\text{\AA}$<br>L(002, 202) | %<br>$X_c$ |
|-------------------|----------------|------------------------|-----------------------------|------------------------|-----------------------------|------------|
| $N_y$             | Nylon-6        | 4.373                  | 3.719                       | 132                    | 125                         | 30         |
| $M_1$             | Nomex 1%       | 4.372                  | 3.719                       | 133                    | 120                         | 33         |
| $M_2$             | Nomex 3%       | 4.373                  | 3.719                       | 134                    | 119                         | 34         |
| $M_3$             | Nomex 5%       | 4.373                  | 3.719                       | 132                    | 117                         | 36         |
| $M_4$             | Nomex 10%      | 4.373                  | 3.719                       | 132                    | 110                         | 39         |
| $M_5$             | Nomex 15%      | 4.372                  | 3.719                       | 134                    | 109                         | 37         |
| $M_6$             | Nomex 20%      | 4.372                  | 3.719                       | 134                    | 109                         | 35         |
| $B_{T1}$          | Triblock 10%   | 4.360                  | 3.701                       | 127                    | 107                         | —          |
| $B_{M1}$          | Multiblock 10% | 4.365                  | —                           | 110                    | —                           | —          |

<sup>a</sup>  $M_1$ - $M_6$ , polyblends of nylon-6-Nomex;  $B_{T1}$ ,  $B_{M1}$ , triblock and multiblock copolyamides (Nomex content of 10 wt %).

diphenylsufone terephthalamide) (PSA) in our previous paper.<sup>5,6</sup>

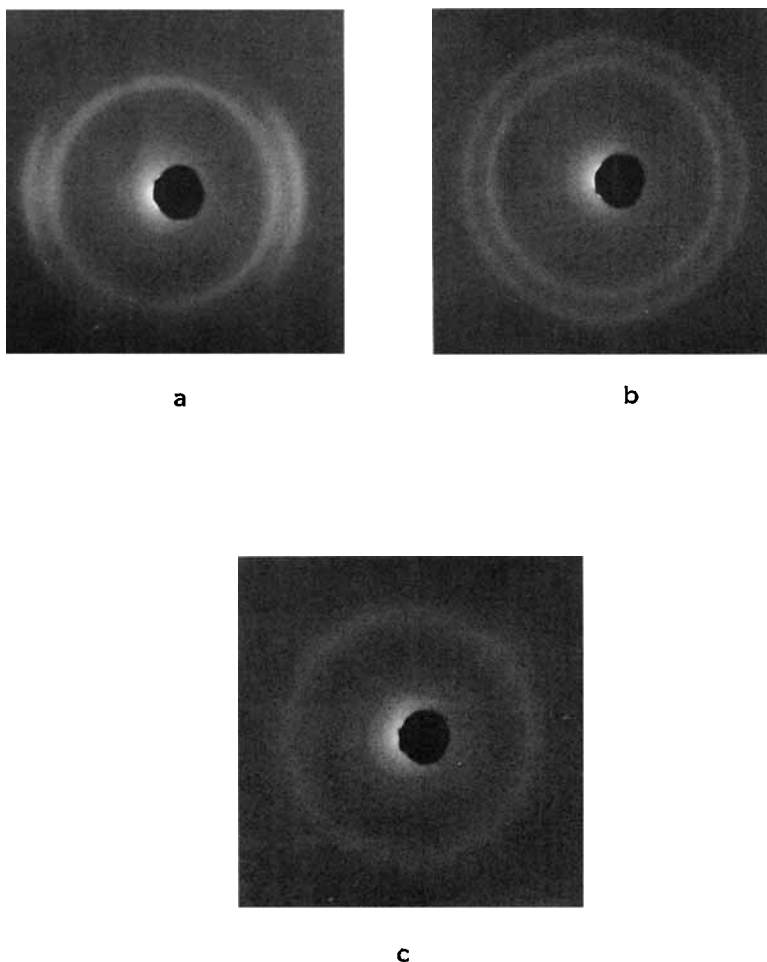
From the WAXS diffraction patterns in Figure 3 and Figure 4, it was found that the nylon-6/Nomex blends ( $M_1$ - $M_6$ ) all had two diffraction peaks, i.e.,  $2\theta = 20.5$  and  $24^\circ$ , and also the triblock copolyamides. However, the multiblock copolyamides had only one at  $2\theta = 20^\circ$ , evidently indicating a new crystal structure of multiblock copolyamides formed, i.e., the (200) plane of nylon-6-Nomex multiblock copolyamide in a structure of nylon-6 formed a new crystal structure.

### Morphological Observation

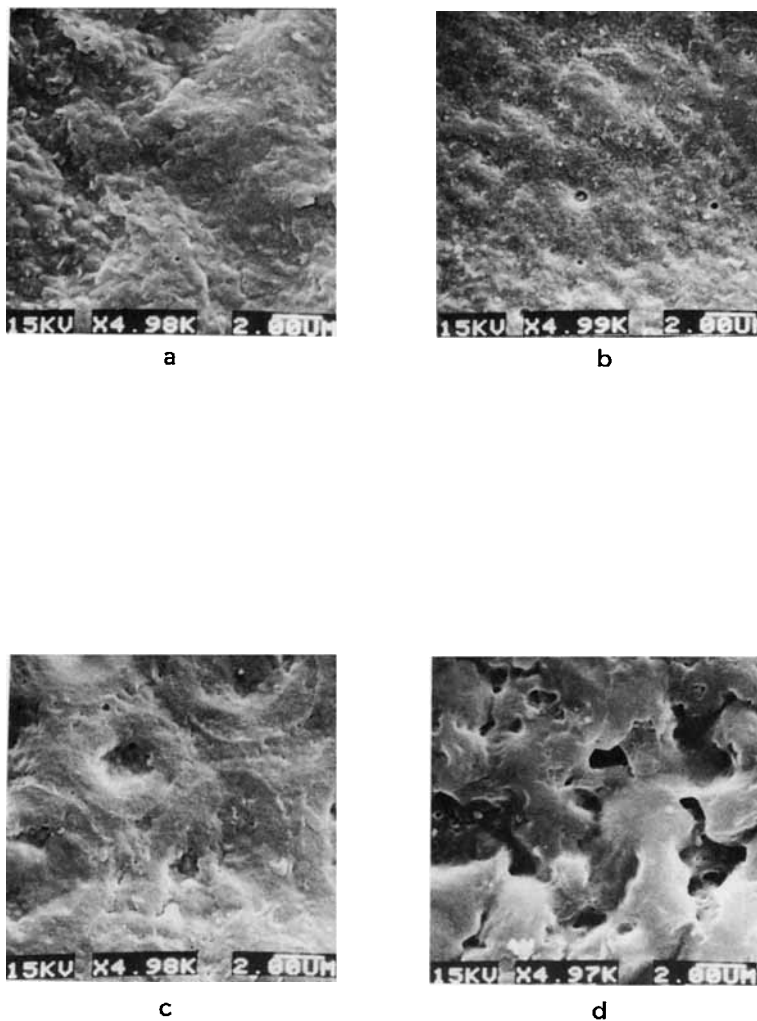
Scanning electron microscopy (SEM) was used to visualize the microstructure of the polyblends and copolymers. Photomicrographs in Figure 5 show a uniform surface structure for the nylon-6 homo-

polymer, but the polyblends showed a dispersed grain size as the amount of Nomex was increased [Figures 5(a) and (b)]. The grain particles were considered to be aggregates of Nomex.

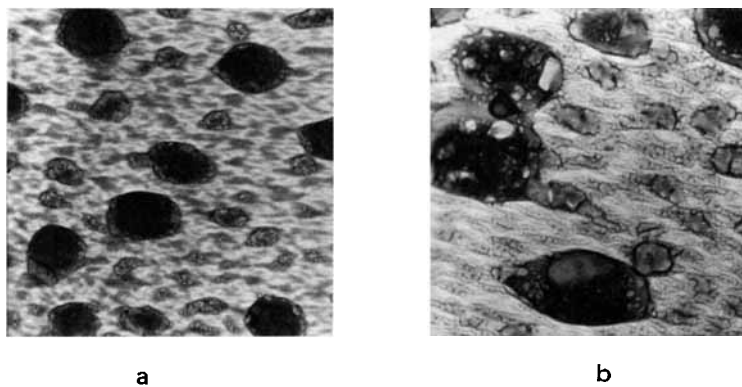
The SEM of a polyblend of nylon-6 with 10 wt % of Nomex and its extract of surface Nomex from the blend [using *N,N*-dimethylacetamide (DMAc) as solvent at  $50^\circ\text{C}$  for 24 h] are shown in Figure 5(c). The surface structure of the treated blend exhibited an orderly void structure, and was evidently different from that of the untreated film. The SEM of a polyblend also with 10 wt % of Nomex and its extract of surface nylon-6 from the blend [using formic acid (HCOOH) as solvent and at room temperature for 8 h] are shown in Figure 5(d). This indicates that the dispersed phase of Nomex in the polyblend is less compatible with nylon-6 and has a tendency to decrease its interfacial area.<sup>17</sup> From the transmission electron micrograph (TEM) anal-



**Figure 4** WAXD patterns of nylon-6 and block copolymer: (a), nylon-6; (b), triblock copolymer; (c), multiblock copolymer.

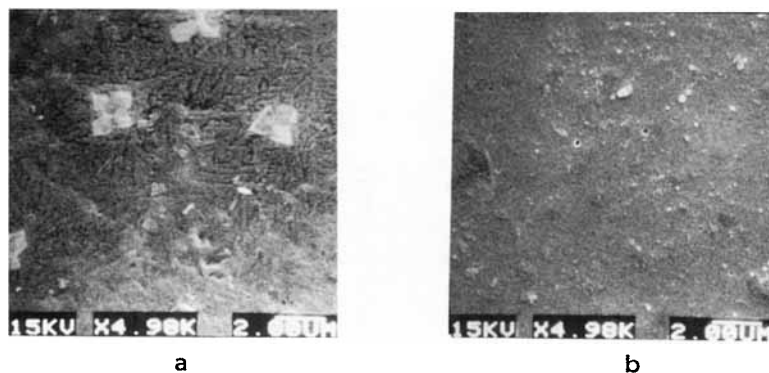


**Figure 5** SEMs of: (a), blend of nylon-6 with Nomex 5 wt %; (b), Nomex 10 wt %; (c), surface structure of nylon-6/Nomex (95 : 5) remained after extraction of Nomex from the blend with DMAc; (d), blend of nylon-6 with Nomex 5 wt % after extraction of nylon-6 from the blend with formic acid.



**Figure 6** TEMs of blend of nylon-6 with 10 wt % Nomex: (a), 5,000 $\times$ ; (b), 16,000 $\times$ .





**Figure 7** SEMs of: (a), triblock copolyamide of 15 wt % Nomex content; (b), multiblock copolyamide of 15 wt % Nomex content.

ysis, it is shown in Figures 6(a) and (b) that the morphology of Nomex in the nylon-6/Nomex blends exhibits a dispersed grain particle structure. This structural feature was quite different from those observed in the poly-*p*-benzamide (PBA) or poly-*p*-phenylene terephthalamide (PPTA), which have liquid crystal behavior and a tendency to form a higher-order microfibrillar structure when dispersed in the matrix of nylon-6.<sup>2,3</sup>

It is seen in Figures 7(a) and (b) that the morphology of triblock and multiblock copolyamides exhibits a more homogeneous texture rather than an aggregated one.

### Mechanical Properties of Polyblends and Copolymers

Mechanical properties of polyblends and block copolymers are presented in Table V, Figure 8, and Figure 9. The tensile strength ( $T_b$ ) and the initial modulus ( $M_i$ ) of various polyblends of nylon-6 ( $M_1$ – $M_6$ ) were found to progressively increase as the content of Nomex was increased. This trend may result from the immobility and rigidity of the aggregated Nomex domain, and also the increase of tie molecules connecting intercrystalline or intracrystalline regions among nylon-6 polymer chains.<sup>18,19</sup> Plastic deformation of the blends was reduced due to the restraint of the wholly rigid Nomex molecules so the yield strength was enhanced, but the ultimate elongation decreased. Moreover, it was observed that the blends containing more than 10 wt % Nomex exhibited a continuous reduction of mechanical properties, finally down to complete brittleness.

The effects on mechanical performance of incorporating the Nomex block segment in copolymers ( $B_T$ ,  $B_M$ ) are given in Figure 9. It was found that

the multiblock copolyamide prepared by using P-APA as a coupling agent had much better tensile strength and elongation than that of the polyblend with the same amount (10 wt %) of Nomex. Nevertheless, data for triblock copolyamide still lay between nylon-6 and Nomex homopolymer. The ordered block copolyamides had better properties not only due to the introduction of wholly rigid units, which caused a higher intramolecular stiffness, but also the increase of the intermolecular forces between polymer chains, therefore forming a more uniform and compatible structure.

**Table V** Mechanical Properties of Nylon-6–Nomex Polyblends and Block Copolyamides

| Code <sup>a</sup>                        | Nomex wt %         | $T_b$ (MP <sub>a</sub> ) | $E_b$ (%) | $M_i$ (GP <sub>a</sub> ) |
|--|--------------------|--------------------------|-----------|--------------------------|
| $N_y$                                    | 0                  | 45.19                    | 44.0      | 0.88                     |
| $M_1$                                    | 1                  | 48.50                    | 27.8      | 1.05                     |
| $M_2$                                    | 3                  | 52.21                    | 27.1      | 1.29                     |
| $M_3$                                    | 5                  | 55.42                    | 21.2      | 1.41                     |
| $M_4$                                    | 10                 | 63.85                    | 13.7      | 1.58                     |
| $M_5$                                    | 15                 | 60.73                    | 8.5       | 1.63                     |
| $M_6$                                    | 20                 | 59.02                    | 5.9       | 1.67                     |
| <sup>a</sup> polyblends of nylon 6-Nomex |                    |                          |           |                          |
| Code                                     | Polymer            | $T_b$ (MP <sub>a</sub> ) | $E_b$ (%) | $M_i$ (GP <sub>a</sub> ) |
| $N_m$                                    | Nomex <sup>a</sup> | 70.0                     | 11.2      | 9.26                     |
| $B_{M1}$                                 | Multiblock 10%     | 78.93                    | 15.6      | 8.98                     |
| $B_{T1}$                                 | Triblock 10%       | 44.17                    | 23.0      | 2.95                     |
| $N_y$                                    | Nylon-6            | 45.19                    | 44.0      | 0.886                    |

$T_b/E_b/M_i$  = breaking tensile strength/elongation/initial modulus.

<sup>a</sup> From Ref. 8.

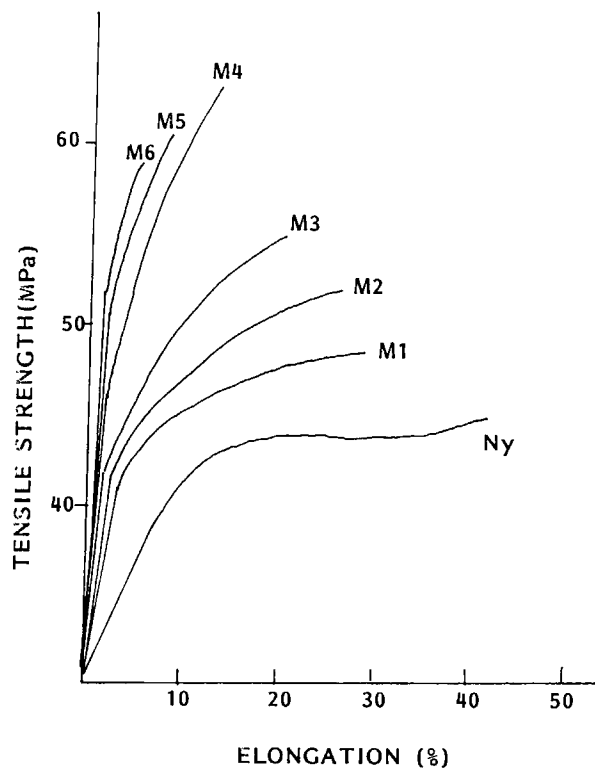
## CONCLUSIONS

Six nylon-6/Nomex polyblends were prepared by physical blending and six nylon-6-Nomex triblock and multiblock copolyamides were synthesized by chemical extension using P-APA as a coupling agent. The reinforcement of nylon-6 with wholly rigid PmIA (Nomex) proved to be successful. Multiblock copolymers showed, for the same content of Nomex, better mechanical properties than those of polyblends and triblock copolyamides.

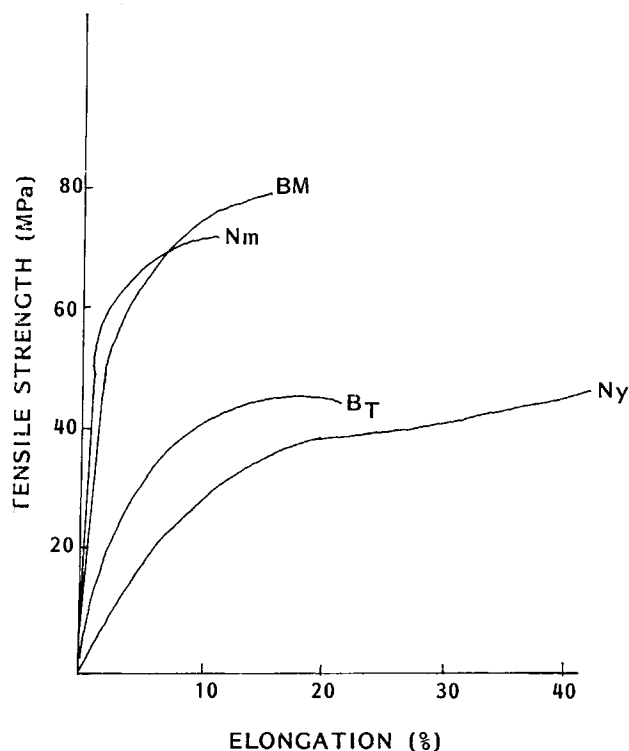
From the morphological features, it was demonstrated that the disperse-phase structure was observed in both polyblends and triblock copolyamide, whereas the multiblock copolyamides exhibited a more homogeneous, compatible structure.

From DSC analysis, it was shown that wholly rigid Nomex reinforced nylon-6 polyblends exhibited higher glass transition temperatures than that of nylon-6 homopolymer, which increased with the increase of Nomex content. The  $T_g$  and  $T_m$  of multiblock copolyamides were even higher than those of polyblends and triblock copolyamides.

Analysis by X-ray diffraction showed that the



**Figure 8** Stress-strain curves for polyblends of nylon-6 with Nomex wt % of: ( $N_y$ ), 0; ( $M_1$ ), 1; ( $M_2$ ), 3; ( $M_3$ ), 5; ( $M_4$ ), 10; ( $M_5$ ), 15; ( $M_6$ ), 20.



**Figure 9** Stress-strain curves for copolyamides: ( $N_y$ ), nylon-6; ( $N_m$ ), Nomex; ( $B_T$ ), triblock copolyamide of 10 wt % Nomex; ( $B_M$ ), multiblock copolyamide of 10 wt % Nomex.

polyblends, triblock copolyamides, and nylon-6 homopolymer had two diffraction peaks, i.e.,  $2\theta = 20.5$  and  $24^\circ$ . However, the multiblock copolyamides had only one at  $2\theta = 20^\circ$ , indicating a different crystal structure of multiblock copolyamides. Also, data showed an increase in crystallinity and reduction in crystallite size in the  $\alpha$  (002, 202) plane of nylon-6 matrix, which gradually increased with the increase of Nomex content. The optimum Nomex content in the nylon-6 was considered to be 10 wt %.

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