Modification of Nylon-6 with Semirigid Poly(p-diphenylmethyl terephthalamide)

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SYNOPSIS

In this research, flexible nylon-6 was reinforced by semirigid aromatic polyamide poly(p-diphenylmethyl terephthalamide) (PMA) through physical polyblending and chemical copolymerization using p-aminophenylacetic acid (P-APA) as a coupling agent. From the DSC measurement, it was shown that the T_g of the polyblends was increased with the increase of PMA content. It was discovered that the T_g and T_m of multiblock copolyamides would be higher than those of polyblends and triblock copolyamides. The multiblock copolyamides exhibited a homogeneous texture rather than an aggregated one. Scanning electron microscopy revealed that the polyblends were a dispersed-phase structure. We found that from the wide-angle X-ray diffraction pattern the triblock copolyamides and polyblends had two diffraction peaks, i.e., $2\theta = 20°$ and $24°$. However, the multiblock had only one at $2\theta = 20°$, which evidently indicates that a new crystal structure of multiblock copolyamides was formed. As for the mechanical properties, the multiblock copolyamides were found to have more significant reinforcing effects than those of polyblends and triblock copolyamides. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Recently, a number of attempts were made to increase the mechanical properties of the aliphatic nylons through the physical blending and chemical modification of aromatic polyamides such as Kevlar, polybenzamide (PBA),[1-5] or poly(4,4-diphenylsulfone terephthalamide) (PSA).[6,7] As shown in our previous papers,[6-8] the aliphatic nylon-6 when modified by the semirigid PSA or wholly rigid Nomex exhibited better thermal and mechanical properties. In this study, we used semirigid polyamide poly(p-diphenylmethyl terephthalamide) (PMA) to reinforce the aliphatic nylon-6. The chemical structure of PMA is as follows:
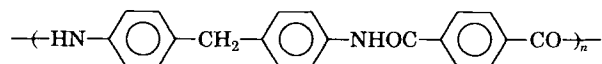
The semirigid PMA has the same monoclinic crystal structure[9-14] as that of nylon-6.

EXPERIMENTAL

Materials

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°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.[15]
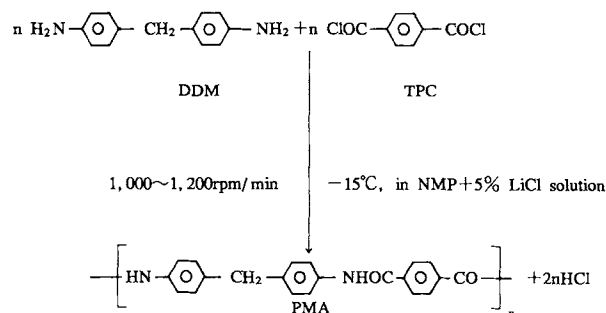
Terephthaloyl dichloride (TPC), 4,4'-diaminodiphenyl methane (DDM), and p-aminophenylacetic acid (P-APA) were purchased from Merck Co. and used as received.

N-Methyl-2-pyrrolidone (NMP) was first distilled over CaH_2 at 92–94°C/14 mmHg and then stored over 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°C for 5 h.

Preparation of Polyamides and Their Prepolymers
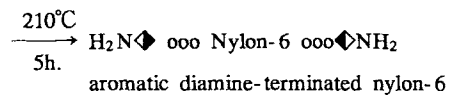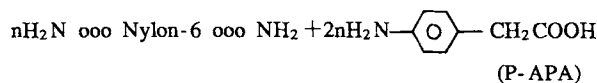
High molecular weight semirigid PMA was polymerized by low-temperature solution polymerization in NMP containing 5% LiCl at $-15°C$ for 30 min.[6-8]The reaction scheme is shown as follows:

n H₂N—⟨O⟩— CH₂—⟨O⟩— NH₂ +n ClOC—⟨O⟩—COCl

DDM   TPC

1,000~1,200rpm/min $-15°C$, in NMP+5% LiCl solution

—[HN—⟨O⟩— CH₂—⟨O⟩— NHOC—⟨O⟩-CO—]ₙ +2nHCl

PMA

Similarly, the low molecular weight PMA was also prepared by excess TPC with DDM in NMP + 5% LiCl solution, i.e.,

ClOC ▮▯▮▯ PMA ▮▯▮▯ COCl

PMA prepolymer

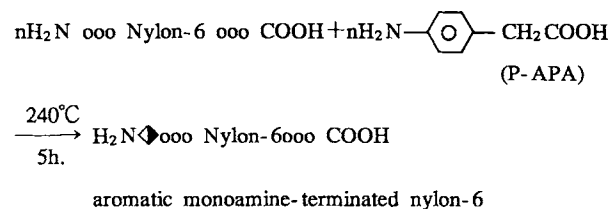▮▯▮▯ : semi-rigid chain segment of PMA.
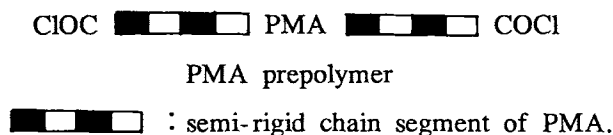
A low molecular weight diamine-terminated nylon-6 prepolymer was prepared by an excess of hexamethylene diamine (HMDA) as described in the literature.[16,17] The prepolymer was reacted with P-APA coupling agent at 210°C for 5 h. The product was purified and dissolved in an NMP + 5% LiCl solution for further use:

nH₂N ooo Nylon-6 ooo NH₂ +2nH₂N—⟨O⟩— CH₂COOH

(P-APA)

210°C
⟶ H₂N◆ ooo Nylon-6 ooo◆NH₂
5h.

aromatic diamine-terminated nylon-6

—◆— : P-APA monomer.

The long-chain monoamine-terminated nylon-6 prepolymer was also prepared by bulk polymerization at 240°C for 5 h. The reaction scheme is illustrated as follows:

nH₂N ooo Nylon-6 ooo COOH+nH₂N—⟨O⟩— CH₂COOH

(P-APA)

240°C
⟶ H₂N◆ooo Nylon-6ooo COOH
5h.

aromatic monoamine-terminated nylon-6

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

Synthesis of Nylon-6-PMA Block Copolymers

The copolyamides were synthesized by reacting of the nylon-6 prepolymer with the PMA prepolymer using the following procedure. The aromatic diamine-terminated nylon-6 prepolymer ($\bar{M}_n = 1300$) or monoamine-terminated nylon-6 prepolymer ($\bar{M}_n = 10,700$) in NMP + 5% LiCl (A bath) and the aramid PMA prepolymer ($\bar{M}_n = 1180$) also in NMP + 5% LiCl (B bath) were allowed to mix and stirred vigorously in N_2 atmosphere system at $-5°$ to $10°C$ for 30 min, then raised to room temperature and stirred continuously for 1 h. Finally, a homogeneous 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:

Table I Characteristics of Prepolyamides and PMA

Polymer[a]	N6 Prepolymer	N6ₐ Prepolymer	PMA Prepolymer	PMA
$\bar{M}_n{}^{[b]}$	998	1300	1180	1.32×10^5 [c]

[a] N6: amine-terminated nylon-6 prepolymer (by HMDA). N6ₐ: aromatic diamine-terminated nylon-6 prepolymer (by P-APA). Elemental analysis (%): C, (64.2); H, (9.6); N, (12.5).
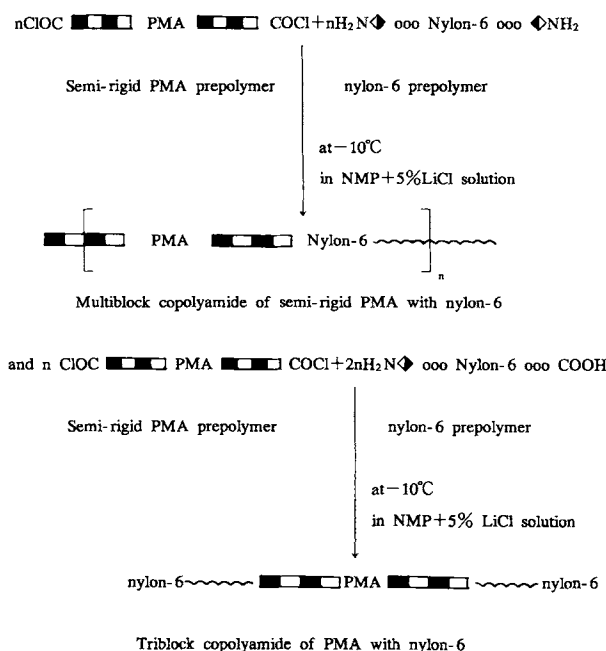[b] $\bar{M}_n = 15.600 \times \eta_{inh}^{1.49}$ according to the literature.[8]
[c] From GPC measurement.

Table II   Characteristics of Block Copolyamides

Code[a]	Polymer	PMA (wt %)	Reaction Time (h)	η_{inh}[b]
B_{M1}	N6-b1-PMA	10	0.5	1.15
B_{M2}	N6-b2-PMA	20	0.5	1.44
B_{T1}	N6a-PMA-N6a	10	0.5	1.25
B_{T2}	N6a-PMA-N6a	20	0.5	1.46
N6	Nylon-6 prepolymer	0	—	0.11
N6a	Long-chain nylon-6	0	—	0.78

[a] B_{M1}-B_{M2}: multiblock copolymer: B_{T1}-B_{T2}: triblock copolymer by the use of P-APA coupling agent. N6: amine-terminated nylon-6 prepolymer ($\bar{M}_n \doteqdot 1000$). N6a: aromatic monoamine-terminated nylon-6 prepolymer ($\bar{M}_n = 10{,}700$, measured in m-crescol at 25°C).[8]

[b] Measured at a concentration of 0.5 g dL^{-1} in NMP + 5% LiCl at 30°C.

nClOC ▇▢▇▢ PMA ▇▢▇▢ COCl+nH₂N◆ ooo Nylon-6 ooo ◆NH₂

Semi-rigid PMA prepolymer   nylon-6 prepolymer

at−10°C

in NMP+5%LiCl solution

▇▢▇▢ PMA ▇▢▇▢ Nylon-6 〰〰〰]ₙ

Multiblock copolyamide of semi-rigid PMA with nylon-6

and n ClOC ▇▢▇▢ PMA ▇▢▇▢ COCl+2nH₂N◆ ooo Nylon-6 ooo COOH

Semi-rigid PMA prepolymer   nylon-6 prepolymer

at−10°C

in NMP+5% LiCl solution

nylon-6〰〰〰 ▇▢▇▢PMA ▇▢▇▢ 〰〰〰nylon-6

Triblock copolyamide of PMA with nylon-6

The various multiblock and triblock copolyamides were prepared by a low-temperature polymerization of nylon-6 prepolymer with different amounts (wt %) of semirigid PMA prepolymers. The inherent viscosities of the block copolyamides were seen to be greater than those of the prepolymers, indicating that the block copolyamides were of higher molecular weight. In general, the chain-extending reaction could be completed in 10–15 min and yield as high a molecular weight copolymer as those of nylon-6–PSA copolyamides in our previous paper.[6,7] All the nylon-6–PMA copolyamides are summarized in Table II.

Blends of Aramid PMA and Nylon-6

In this study, the high molecular weight nylon-6 ($\bar{M}_n = 21{,}500$) was blended physically with various ratios (1, 5, 10, 15, and 20%) of high molecular weight semirigid PMA as described by Takayanagi et al.[1-5] The mixtures were dissolved in 98% H_2SO_4. The clear, single-phase solutions were cast 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.

Measurements

Infrared spectra of homopolymers and copolymers were obtained by a Hitachi Model 260-50 Type, over a range 400–4,000 cm^{-1}. The samples were in a form of film about 10 μm thickness.

Elemental analysis (C, H, N) was performed by Heraeus CHN-O-Rapid Analyzer. A differential Scanning Calorimeter (DSC) was used to measure the temperature of crystallization (T_c) and the degree of crystallinity (X_c) in a nitrogen atmosphere with a DuPont 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 CuKα 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 data was obtained on the Instron 1122 Type testing instrument at an extension rate of 5 mm/min and full load of 50 kg.

RESULTS AND DISCUSSION

Analysis of Infrared Spectra

Infrared spectra were obtained from using the thin-film technique. The transmission IR spectra of homopolymers and block copolymers are shown in Figure 1. The IR spectrum of nylon-6 (curve N_y) was characterized at 3,300 cm^{-1} ($=N-H$ stretch vibration), 1,650 cm^{-1} ($=C=O$), 1,560 cm^{-1} ($=N-H$ deformation), and 2,900 and 2,770 cm^{-1} ($-CH_2-$ stretch vibration) absorptions.

The characteristic IR spectrum of PMA (cure Pm) was shown at 1,530 cm^{-1} ($-C_6H_4$-$CH_2-C_6H_4-$), 1,660 cm^{-1} ($-CONH-$), and 1,100 cm^{-1}, 800 cm^{-1} ($-C_6H_4-$ on parasubstituted) absorptions.

The nylon-6–PMA block copolymers (curve B_{M1}) did show both the characteristic absorption of nylon-6 and PMA. Noticeable was a characteristic absorp-

tion of the aliphatic $-CH_2-$ at 2900, 2,770, and 1,530 cm^{-1} ($-C_6H_4-CH_2-C_6H_4$) for the block copolymers with P-APA as a coupling agent.

Thermal Properties of Block Copolymers and Polymer Blends

Polymers with an aromatic ring structure could contribute to their thermal stability. Through this study, the presence of aromatic PMA 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/PMA (M_1–M_5) was increased with the increase of PMA wt % content. This indicates that the micro-Brownian motion of amorphous nylon-6 chains did suffer from the restraint of the semirigid PMA molecules, especially if the amounts of PAM were increased. Surprisingly, it was found that the T_m of polyblends did not change much. It still remained at about 219°C for the nylon-6/PMA series (M_1–M_5). This result was also seen in our previous work for nylon-6/PSA and Nomex/
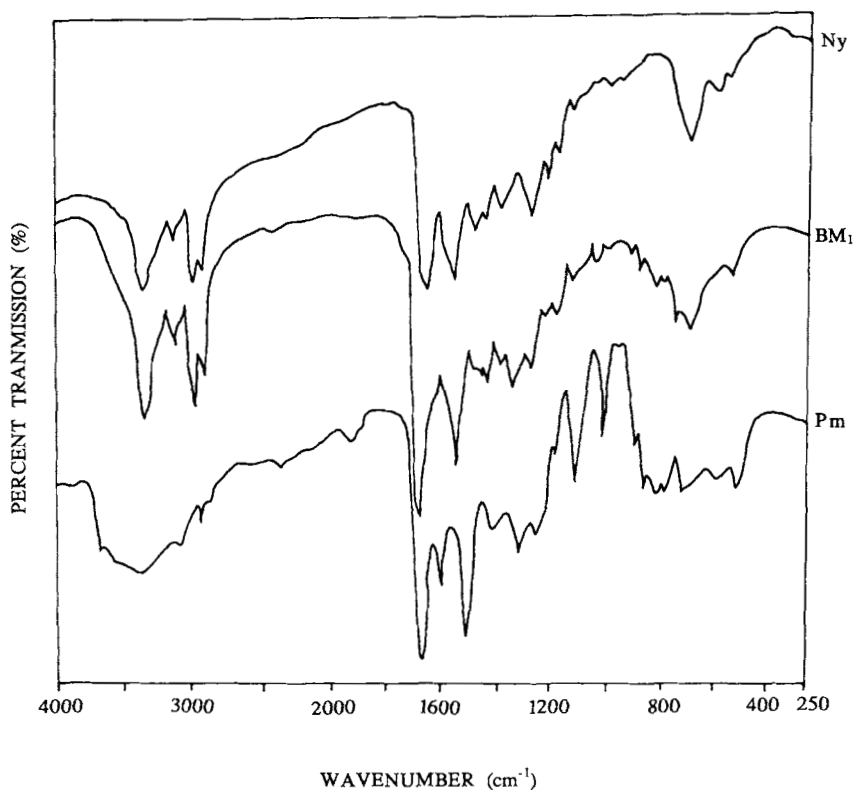

Figure 1   Infrared spectra of homo- and copolyamide films: (N_y) nylon-6 homopolymer; (P_m) PMA homopolymer; (B_{M1}) multiblock copolyamides of PMA 10%.
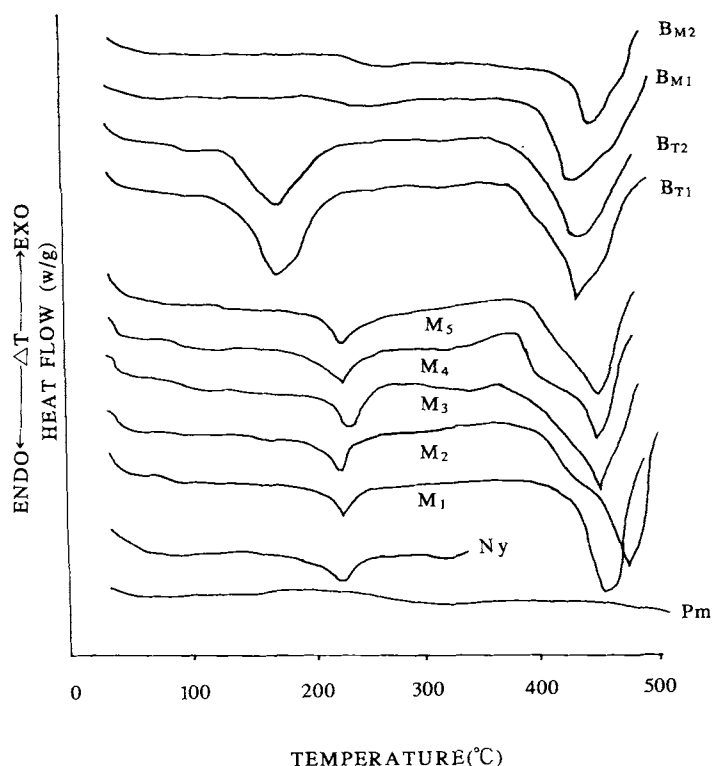
Figure 2 DSC plots of polyblends of nylon-6 with PMA and nylon-6–PMA block copolymers in nitrogen: (P_m) PMA; (N_y), nylon-6; (M_1), PMA 1%; (M_2), PMA 5%; (M_3), PMA 10%; (M_4), PMA 15%; (M_5), PMA 20%; (B_{T1}, B_{T2}), triblock copolyamide of 10 and 20 wt % PMA content; (B_{M1}, B_{M2}), multiblock copolyamide of 10 and 20 wt % PMA content.

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

Code	Polymer	T_g (°C)	T_m (°C)	X_c (%)	ΔH_{fus} (J/g)
Ny	Nylon-6	67	219	24	43
Pm	PMA	300	> 500	—	—
M_1	PMA 1%	84	219	26	49
M_2	PMA 5%	90	219	29	55
M_3	PMA 10%	98	220	36	68
M_4	PMA 15%	100	219	34	65
M_5	PMA 20%	125	219	33	62
B_{T1}[a]	Triblock 10%	83	160	—	—
B_{T2}[a]	Triblock 20%	85	161	—	—
B_{M1}[b]	Multiblock 10%	227	425	—	—
B_{M2}[b]	Multiblock 20%	235	448	—	—

[a] B_{T1}, B_{T2}: triblock copolyamide (PMA content of 10 and 20 wt %).

[b] B_{M1}, B_{M2}: Multiblock copolyamide (PMA content of 10 and 20 wt %).

[c] M_1–M_5: polyblends of nylon-6 with PMA.

nylon-6 polyblends.[6-8] It also indicates that the PMA 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.[1] It is also consistent with our previous work for PSA/nylon-6 and Nomex/nylon-6 polyblends[6-8] 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):

$$X_c = \frac{\Delta H_\delta}{\Delta H_f} \times 100\% \qquad (1)$$

where X_c is the degree of crystallinity for specimens; ΔH_δ (J/g), the heat capacity for specimens under investigation; and ΔH_f, the heat of fusion for 100% crystalline nylon-6, which was 189 J/g.[18,19] From Table III, it was shown that the degree of crystallinity increased as the proportion of PMA was increased. However, the polymer blend with 15 wt %

Table IV   *d*-Spacing, Crystallite Size, and Degree of Crystalline of Nylon-6–PMA Polyblends, and Block Copolyamide

Code[a]	Polymer	Å *d* (200)	Å *d* (002, 202)	Å L (200)	Å L (002, 202)	% X_c
N_y	Nylon-6	4.373	3.719	132	125	30
M_1	PMA 1%	4.36	3.70	135	125	34
M_2	PMA 5%	4.37	3.70	133	124	35
M_3	PMA 10%	4.37	3.70	135	120	39
M_4	PMA 15%	4.39	3.70	132	117	38
M_5	PMA 20%	4.38	3.70	134	110	37
B_{T1}	Triblock 10%	4.55	3.78	—	—	—
B_{M1}	Multiblock 10%	4.33	—	120	—	—

[a] M_1–M_5: polyblends of nylon-6 with PMA.
[b] B_{T1}, B_{M1}: triblock and multiblock copolyamides (PMA content of 10 wt %).

of PMA exhibited a decrease of crystallinity. This suggests that the addition of excess amounts of PMA could result in a decrease of the thermal mobility of nylon-6 due to the restraint of the immobile and semirigid PMA segments.
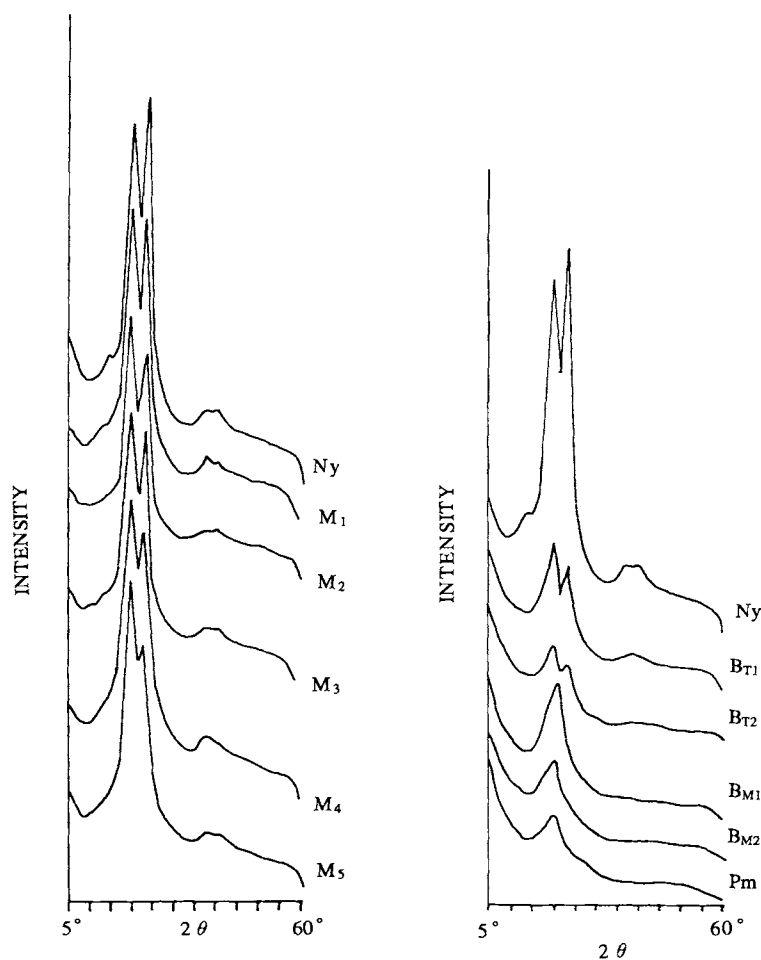
It is also shown in Figure 2 and Table III that

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

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 exhibited 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. The glass transition temperature (T_g) of multiblock co-

polyamides showed only one peak; therefore, a compatible state of semirigid PMA with nylon-6 could be possible in the multiblock copolymer. From the result of DSC analysis, it is found that the melting temperature of the multiblock copolyamides was up to 400°C. Its block copolyamides also exhibited higher T_g and T_m because that of the nylon-6-PMA multiblock copolyamide had formed a new crystal structure.
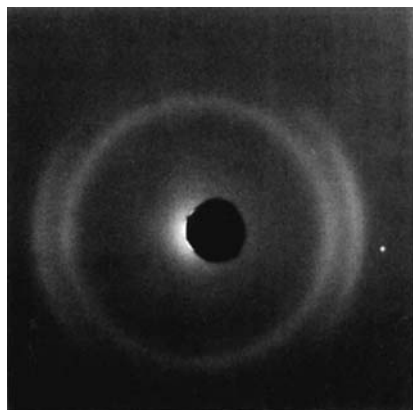

(a)
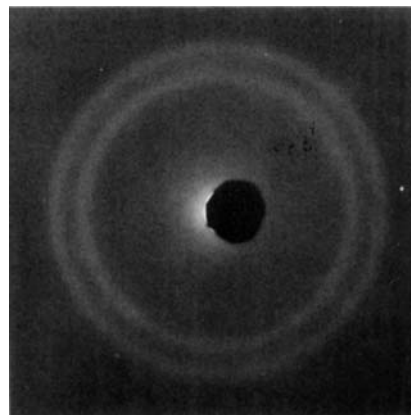
(b)
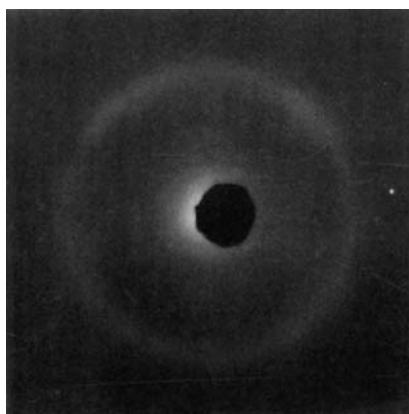
(c)

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

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 semirigid PMA, the crystallite size of nylon-6 apparently became smaller as the amount of PMA was increased.
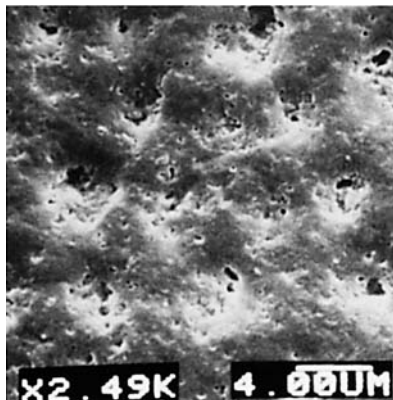
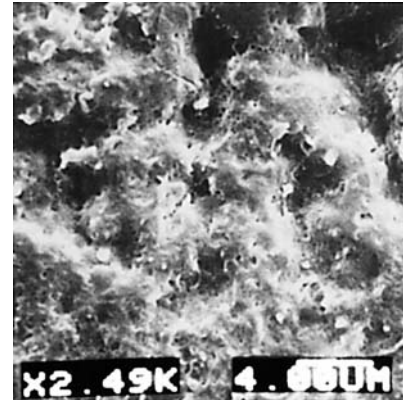Data show an increase in crystallinity and a re-
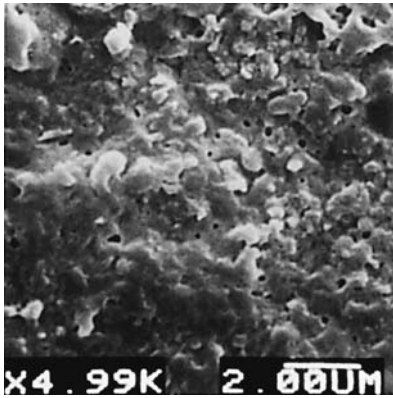
(a)
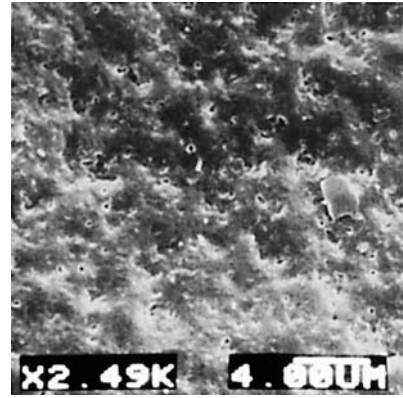
(b)

(c)

(d)

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

duction in crystallite size of nylon-6 matrix in Table IV. However, it should be noted that the crystallite size in the α (002, 202) plane became smaller, but that in the α (200) plane it did not, as semirigid PMA was present. In addition, the d-spacing remained almost a constant value. Thus, it could be concluded that if more content of the aromatic polyamide was blended the more the crystal growth of nylon-6 chain in the α (002, 202) plane could be retarded. The effect of semirigid-chain PMA was the same as that of semirigid-chain poly(4,4'-diphenylsufone terephthalamide) (PSA) and wholly rigid-chain Nomex (PmIA) in our previous paper.[6-8]

From the WAXS diffraction pattern in Figures 3 and 4, it was found that the nylon-6/PMA blends (M_1–M_5) all had two diffraction peaks, i.e., $2\theta = 20°$ and 24°, and also the triblock copolyamides. However, the multiblock copolyamides had only one at $2\theta = 20°$, evidently indicating a new crystal structure of multiblock copolyamides formed, i.e., the (200) plane of nylon-6–PMA multiblock copolyamide in a structure of nylon-6.

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

The SEM of polyblend of nylon-6 with 5 wt % of PMA and its extract of surface PMA from the blend (using N,N-dimethylacetamide [DMA_c] as solvent and at 50°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 the polyblend also with 5 wt % of PMA 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 PMA in the polyblend is less compatible with nylon-6 and has a tendency to decrease its interfacial area.[20] From the transmission electron micrograph (TEM) analysis, it is shown in Figure 6(a) and (b) that the morphology of PMA in the nylon-6/PMA 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 dispersing in the matrix of nylon-6.[2,3]

It is seen in Figure 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

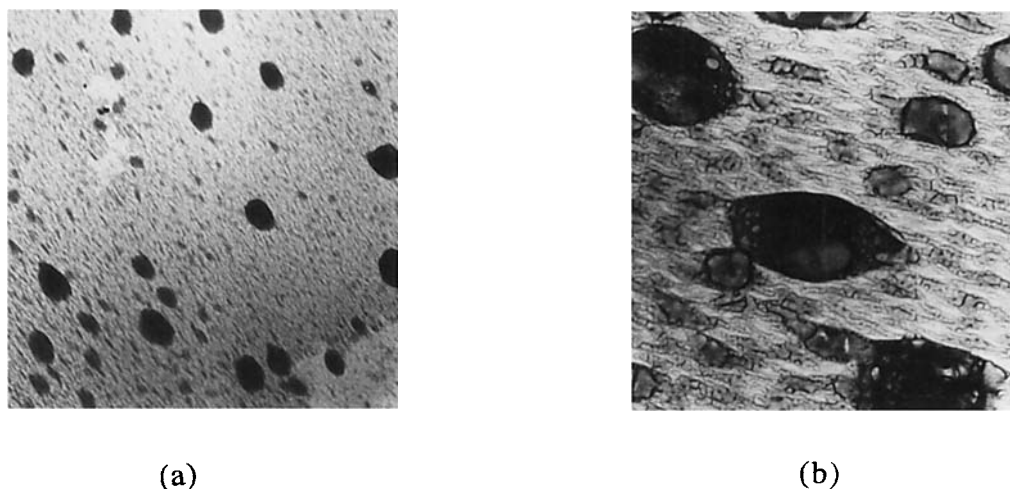Mechanical properties of polyblends and block copolymers are presented in Table V and Figures 8

(a)

(b)

Figure 6   TEM's of blend of nylon-6 with 5 wt % PMA: (a) 100,000×; (b), 20,000×.

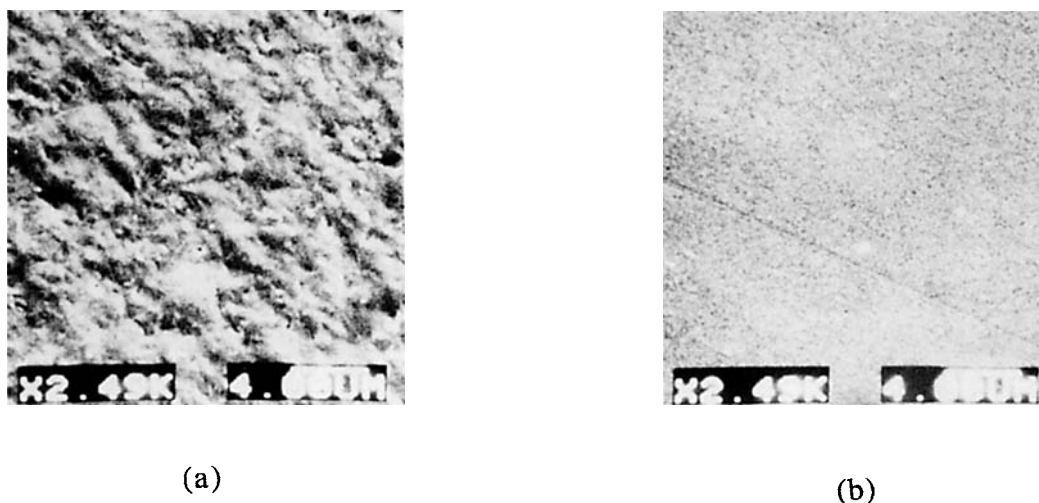**(a)**   **(b)**

Figure 7   SEM's of (a) triblock copolyamide of 15 wt % PMA content; (b) multiblock copolyamide of 15 wt % PMA content.

and 9. The tensile strength (Tb) and the initial modulus (Mi) of various polyblends of nylon-6 (M_1–M_5) were found to be progressively increased as the content of PMA was increased. This trend may have resulted from the immobility and rigidity of the aggregated PMA domain and also from the increase of tie molecules connecting intercrystalline or intracrystalline regions among nylon-6 polymer chains.[21,22]

Plastic deformation of the blends was reduced due to the restraint of the semirigid PMA molecules, so the yield strength was enhanced, but the ultimate elongation decreased. Moreover, it was observed that the blends containing more than 10 wt % PMA exhibited a continuous reduction of mechanical properties down, finally, to complete brittleness.

The effects on mechanical performance of incorporating the PMA block segment in copolymers (B_{T1}, B_{M1}) 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 polyblend with the same amount (10 wt %) of PMA. Nevertheless, data for triblock copolyamide still lay between ny-

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

Code[a]	PMA wt %	Tb (MPa)[c]	Eb (%)[c]	Mi (GPa)[c]
N_y	0	45.19	44.0	0.886
M_1	1	50.17	28.6	1.101
M_2	5	57.63	21.9	1.238
M_3	10	63.73	17.8	1.421
M_4	15	60.34	17.7	1.458
M_5	20	56.05	13.8	1.630

Code[b]	Polymer	Tb (MPa)[c]	Eb (%)[c]	Mi (GPa)[c]
P_m	PMA	64.02	17.0	7.204
B_{M1}	Multiblock 10%	69.06	27.0	5.364
B_{T1}	Triblock 10%	47.23	25.4	3.350
N_y	Nylon-6	45.19	44.0	0.886

[a] M_1–M_5: polyblends of nylon-6 with PMA.
[b] B_T, B_{M1}: triblock and multiblock copolyamides (PMA content of 10 wt %).
[c] $Tb/Eb/Mi$ = breaking tensile strength/elongation/initial modulus.

lon-6 and PMA homopolymer. The ordered block copolyamides had better properties not only due to the introduction of semirigid units, which caused a higher intramolecular stiffness, but also to the increase of the intermolecular forces between polymer chains, therefore forming a more uniform and compatible structure.

CONCLUSIONS

Five nylon-6/PMA polyblends were prepared by physical blending and four nylon-6-PMA triblock and multiblock copolyamides were synthesized by chemical extension using P-APA as a coupling agent. The reinforcement of nylon-6 with semirigid PMA proved to be successful. Multiblock copolymers showed, for the same content of PMA, 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 the DSC analysis, it was shown that the semirigid PMA-reinforced nylon-6 polyblends exhibited higher glass transition temperature (T_g)
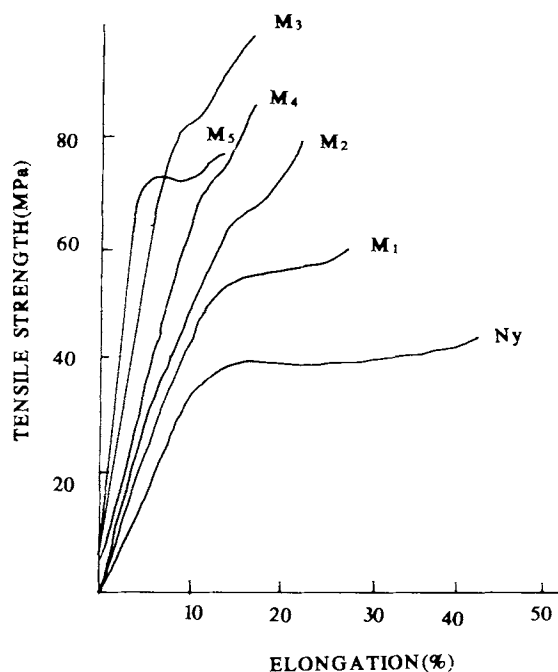

Figure 8   Stress–strain curves for polyblends of nylon-6 with PMA wt % of (N$_y$) 0; (M$_1$) 1; (M$_2$) 5; (M$_3$) 10; (M$_4$) 15; (M$_5$) 20.
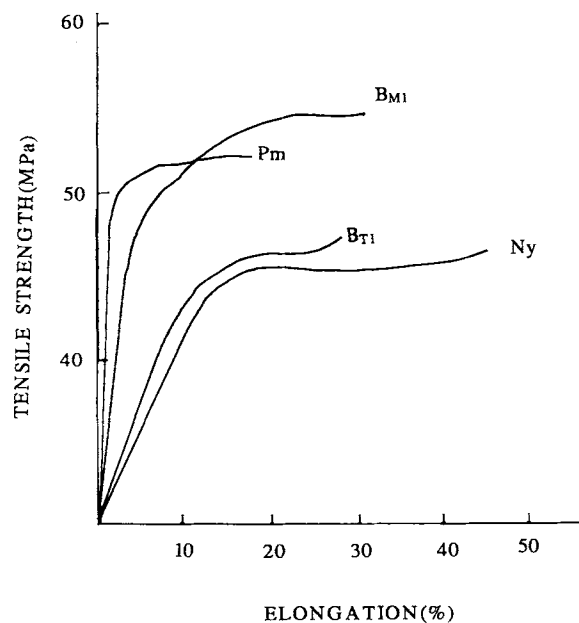

Figure 9   Stress–strain curves for copolyamides: (N$_y$) nylon-6; (P$_m$) PMA; (B$_{T1}$) triblock copolyamide of 10 wt % PMA; (B$_{M1}$) multiblock copolyamide of 10 wt % PMA.

than that of nylon-6 homopolymer, which increased with the increase of PMA content. The T_g and T_m of multiblock copolyamides were even higher than those of polyblends and triblock copolyamides.

Through the analysis of the X-ray diffraction it was shown that the polyblends, triblock copolyamides, and nylon-6 homopolymer had two diffraction peaks, i.e., $2\theta = 20°$ and $24°$. However, the multiblock copolyamides had only one at $2\theta = 20°$, indicating a different crystal structure of multiblock copolyamides. Also, data showed an increase in crystallinity and reduction in crystallite size in the α (002.202) plane of nylon-6 matrix, which gradually increased with the increase of PMA content. The optimum PMA content in nylon-6 was considered to be 10 wt %.

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