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Modification of nylon-6 with semi-rigid and wholly-rigid aromatic polyamides

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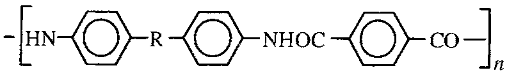
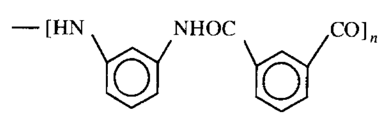
Nylon-6 was reinforced by two semi-rigid aromatic polyamides, poly(*p*-diphenylmethyl terephthalamide) (PMA), and poly(*p*-diphenyloxide terephthalamide) (POA), and also one wholly-rigid aromatic polyamide, poly(*m*-phenylene isophthalamide) (P*m*IA) by physical blending and chemical copolymerization using *p*-amino phenyl acetic acid (P-APA) as a coupling agent. From the results of differential scanning-calorimetry, it was shown that both the polyblends with semi-rigid and wholly-rigid polyamides exhibited a glass transition temperature, T_g, higher than that of nylon-6 homopolymer. It also showed that the T_gs of wholly-rigid polyblends were higher than those of semi-rigid polyblends. Nevertheless, the multiblock copolyamides appeared to have even higher T_g and T_m, and better thermal stability. Morphological observations revealed that all the polymer alloys (polyblends and copolymers) were a dispersed phase structure, although the multiblock copolyamides were more homogeneous and compatible. Based on wide-angle X-ray diffraction, it was found that the polyblends had two diffraction peaks, i.e. $2\theta = 20.5^\circ$ and 24°. However, the multiblock copolyamides had only one peak at $2\theta = 20^\circ$, evidently indicating a new crystal structure of the multiblock copolyamides formed. For the mechanical properties, it was found that the multiblock copolyamides had a more significant reinforcing effect than those of polyblends, especially those copolymerizing with wholly aromatic polyamides.

1. Introduction

Aromatic polyamides are known to be high-performance polymers. Their physical properties and heat stability are superior to those of the aliphatic nylon-6. Therefore, a number of attempts have been made to increase the mechanical properties of the aliphatic nylon by using the physical blending and chemical modification of aromatic polyamides such as kevlar, polybenzamide (PBA) [1–5] or poly(4,4′-diphenylsulphone terephthalamide) (PAS) [6–10]. As shown in our previous papers [6–11], the aliphatic nylon-6 which was modified by the semi-rigid PSA, did exhibit better thermal and mechanical properties. In this work, we extended our experiments further to two other semi-rigid aromatic polyamides, poly(4,4′-diphenylmethyl terephthalamide) (PMA) and poly-(4,4′-diphenyloxide terephthalamide) (POA), and also one wholly-rigid polyamide poly(*m*-phenylene isophthalamide) (P*m*IA). The chemical structures of semi-rigid aromatic polyamides PMA, POA, and PSA, and the wholly-rigid Nomex are shown as [I] and [II] respectively.


(I)

Polymer	PMA	POA	PSA
R	$-CH_2-$	-O-	SO_2-


(II)

Noticeably, the reason for selecting PMA, POA and PSA as the reinforcing part was that the semi-rigid PMA, POA and PSA have the same monoclinic crystal structure as that of nylon-6 [12–17]. Nevertheless, the wholly-rigid Nomex (P*m*IA) has a quite different triclinic crystal structure [18, 19]. This could affect the X-ray diffraction pattern of their polyblend and copolymer.

2. Experimental procedure

2.1. Materials

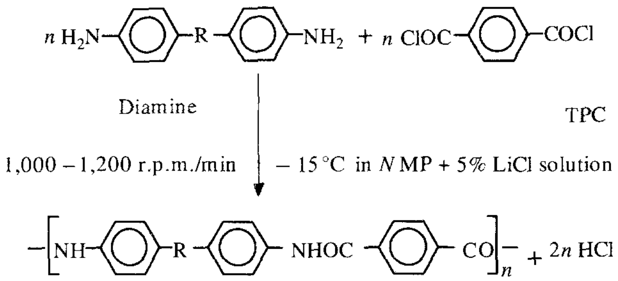
The nylon-6 was obtained from the Formosa Chemical and Fiber Corporation. The sample was first dissolved in formic acid and then poured into a large amount of water. Samples were then refluxed with methanol and hot water for 16 h, and subsequently dried at 100 °C under vacuum for 8 h. Its inherent viscosity ($\eta_{inh} = 1.24$) and M_n (21 500) were obtained according to the literature [20].

4,4′-Diaminodiphenyl methane (DDM), 4,4′-diaminodiphenyl oxide (DDO), and terephthaloyl dichloride (TPC), and also *m*-phenyene diamine(MPA), isophthaloyl dichloride (IPC), and *p*-aminophenyl acetic acid (P-APA) all were purchased from Merck Co., and used as-received.

N-methyl-2-pyrrolidone (*N*MP) was first distilled over CaH_2 at 92–94 °C/14 mm Hg and then stored in the molecular sieves. The moisture content of a 5% LiCl solution in *N*MP was 0.018 wt% as determined by the Karl-Fischer Moisture Meter, MKA-3, Kyoto Electronic. Lithium chloride (LiCl) was dried under vacuum at 160 °C for 5 h.

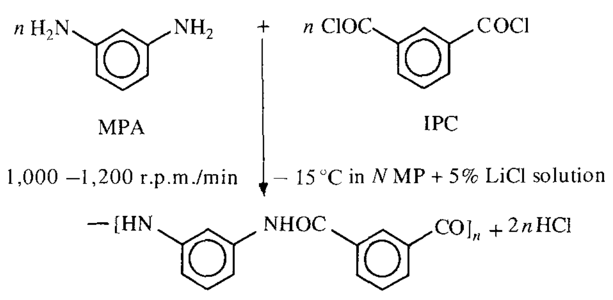
2.2. Preparation of polyamides and their prepolymers

High molecular weight semi-rigid polyamides PMA and POA were polymerized by low-temperature solution polymerization in *N*MP containing 5% LiCl at − 15 °C for 30 min [6, 7, 11]; the reaction scheme is as follows



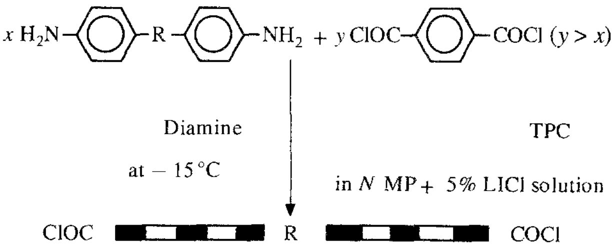
Aramid	PMA	POA
R	$-CH_2-$	$-O-$

In addition, the wholly-rigid Nomex was also synthesized by the same method, as described below



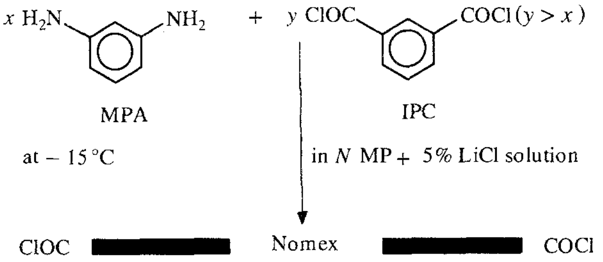
P*m* IA (Nomex)

Low molecular weight semi-rigid acid chloride-terminated aramid PMA and POA were prepared from excess TPC with DDM or DDO in NMP + 5% LiCl solution at a temperature of −10 to −15 °C; the reaction scheme is



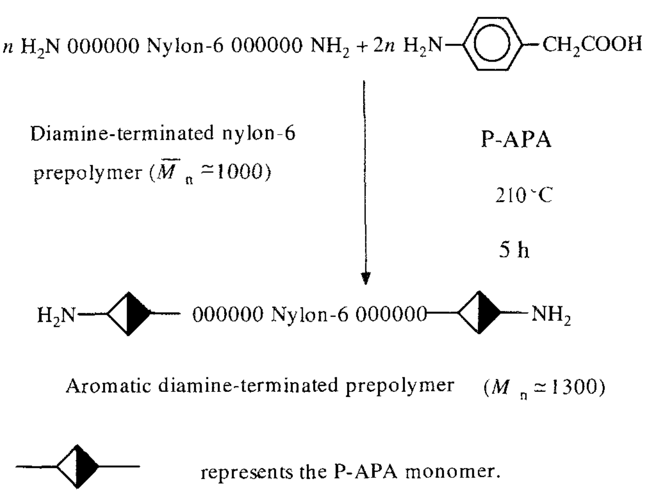
Low molecular weight semi-rigid diacid chloride-terminated aramid prepolymer;■□■□■ represents the semi-rigid chain segment of aramid, and R is $-CH_2-$ or $-O-$.

Similarly, the low molecular weight wholly-rigid Nomex was prepared from excess IPC with MPA in *N*MP + 5% LiCl solution



Low molecular weight wholly-rigid diacid chloride-terminated Nomes prepolymer;▬represents the wholly-rigid chain segment of Nomex.

A low molecular weight diamine-terminated nylon-6 prepolymer was also prepared from an excess of hexamethylene diamine (HMDA) as described in the literature [21, 22]. Then, the prepolymers were further reacted with P-APA coupling agent at 210 °C for 5 h. The products were purified and dissolved in a *N*MP + 5% LiCl solution for further use.



The characteristics of all the synthesis are given in Table 1. M_n and M_w/M_n were determined by water gel permeation chromatography. The solvent was dimethylformamide containing 0.05 mol l^{-1} LiCl. The

TABLE I Characteristics of prepolyamides and aramids

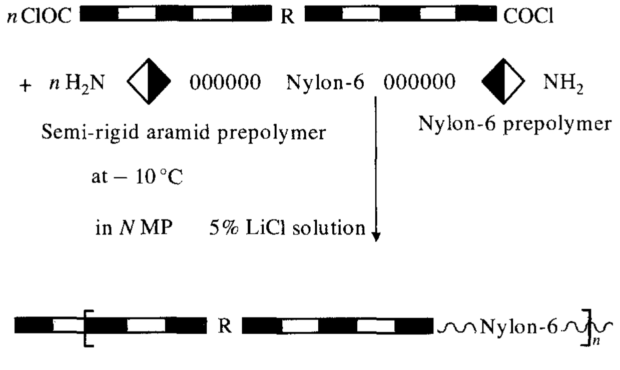
Polymer	$\bar{M}_n$[a]
N6[b]	1300
PSA prepolymer	1380
PMA prepolymer	1180
POA prepolymer	1190
PmIA prepolymer	826
PSA[c]	1.34 × 105
PMA[c]	1.32 × 105
POA[c]	1.35 × 105
PmIA[c]	1.46 × 105

[a] $\bar{M}_n = 15\,600 \times \eta_{inh}^{1.49}$ according to the literature [8].
[b] N6: aromatic diamine-terminated nylon-6 prepolymer (by P-APA). Elemental analysis(%): C(64.2); H, (96); N, (12, 5).
[c] From GPC measurement.

column was μ. BONDANGEL E-Linear which was calibrated at a flow rate of 1 ml min^{-1}.

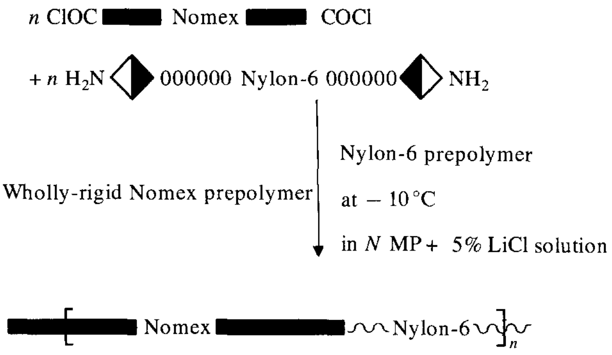
2.3. Synthesis of aromatic polyamide and nylon-6 block copolymers

The copolyamides were synthesized by reacting the nylon-6 prepolymer with the aramid prepolymer as described below. The aromatic diamine-terminated nylon-6 prepolymer ($\bar{M}_n \simeq 1300$) solution in *N*MP + 5% LiCl (A bath) and the aramid prepolymer ($\bar{M}_n \simeq 1000$) PMA, POA or Nomex solution in *N*MP + 5% (B bath) were allowed to mix and stirred vigorously, in a nitrogen atmosphere system at − 5 to − 10 °C for 30 min, then the temperature was raised to room temperature, and the solution stirred continuously for 1 h. Finally, a homogeneous, viscous solution was obtained and poured in to an aqueous solution containing equivalent LiOH. The precipitate was filtered and dried at 80 °C under vacuum for 7 h. Noticeably, all the copolyamides obtained here were dissolved in the *N*MP + 5% LiCl solution, but they were not soluble in formic acid or *m*-cresol, which are good solvents for nylon-6. The detailed reaction schemes are as follows



Multiblock copolyamide of semi-rigid aramid with nylon-6; R is $-CH_2-$ or $-O-$; ▬▭▬▭▬ is the semi-rigid aramid block, and ∿∿∿ is the Aliphatic nylon 6-block.

The copolymerization reaction of wholly-rigid Nomex and nylon-6 prepolymer was as follows



Multiblock copolyamide of wholly-rigid Nomex with nylon-6; ▬ represents the wholly-rigid Nomex block, and ∿∿∿ the aliphatic nylon-6 block.

2.4. Blends of aromatic polyamide and nylon-6

In this study, the high molecular weight nylon-6 ($\bar{M}_n = 21\,500$) was blended physically with various ratios (5%, 10%, 15%, and 20%) of high molecular weight semi-rigid PMA, POA and wholly-rigid Nomex (P*m*IA), as described by Takayanagi *et al.* [1–5]. The mixtures were dissolved in 98% H_2SO_4, and 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 moulded by hot pressing at 240 °C and cooled at a rate of about 15–20 °C min^{-1} to room temperature, and finally annealed at 210 °C for 1 h, in a nitrogen atmosphere.

2.5. Measurements

Infrared spectra of homopolymers and copolymers were obtained using a Hitachi Model 260-50 Type, over the range 250–4000 cm^{-1}. The samples were in the form of a film about 10 μm thick.

Elemental analysis (C, H, N) was performed using a Heraeus CHN–O–Rapid Analyser.

Differential scanning calorimetry (DSC) was used to measure the crystallization temperature, T_c, and the degree of crystallinity, X_c, in a nitrogen atmosphere with a Du Pont model 9900 DSC, at a heating rate of 20 °C min^{-1} to obtain the glass transition temperature, T_g, and the melting temperature, T_m.

Wide-angle X-ray photographs were taken with nickel-filtered CuK_α radiation using Rigaku D/max-II Type X-ray Diffractometer.

A scanning electron microscope, Cambridge steroscan-600, was also used to observe the morphological structure on samples which were sputter-coated with gold to prevent their oxidation.

All stress–strain data were obtained on the Instron 1122 Type testing instrument at an extension rate of 5 mm min^{-1}, and a full load of 50 kg.

3. Results and discussion

Nylon-6–Aramid copolyamides were prepared using P-APA as a coupling agent. Nine nylon-6–aramid copolyamides which were prepared by a low-temperature polymerization of nylon-6 prepolymer with low molecular weight semi-rigid and wholly-rigid aromatic polyamides, are summarized in Table II. To obtain the block copolymers with a high structural order, prepolymers with terminated functional groups were first synthesized prior to the subsequent polymerization. In this study, the various copolyamides were obtained by varying the amounts (wt %) of semi-rigid and wholly-rigid aramid prepolymers. The inherent viscosities of the block copolyamides were found to be greater than those of the prepolymers, suggesting that the block copolyamides had sufficient high molecular weights. 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].

3.1. Analysis of infrared spectra

Infrared spectra were obtained using the thin film technique. The transmission infrared spectra of homopolymer and block copolymer films are shown in Table III and in Fig. 1 (nylon-6–Nomex), Fig. 2 (nylon-6–PMA), and Fig. 3 (nylon-6–POA). As shown in Fig. 1, the nylon-6–Nomex block copolymers (curve B2) showed both the characteristic absorptions of nylon-6 and Nomex. These confirmed that the Nomex segments did link to nylon-6. The infrared spectra of Nomex (curve Nm) are characterized at 3400 cm^{-1} (= N–H stretching vibration), 1680 cm^{-1} (= C = O), 1610 cm^{-1} and 1540 cm^{-1} (C$=\!=\!=$C), and 1450–1650 cm^{-1} (–NHCO– on *meta* substituted), whereas the characteristic infrared spectra of nylon-6 (curve Ny) are shown at 3400 cm^{-1} (= N–H stretching vibration), 1660 cm^{-1} (–CONH–), 1560 cm^{-1} (= N–H deformation), and 2900 and 2770 cm^{-1} (–CH_2– stretching vibration) absorptions.

Similarly, the characteristic absorptions of PMA and POA are shown in Table III. From that, we can conclude that the nylon-6–PMA and nylon-6–POA the block copolymers did show a chemical linkage of nylon-6 and PMA and POA prepolymers.

TABLE II Characteristics of block copolyamides

Code[a]	Polymer[a]	Aramid (wt %)	Reaction time (h)	η_{inh}[b]
B1	N6–b1–P*m*IA	10%P*m*IA	1/2	1.26
B2	N6–b2–P*m*IA	15%P*m*IA	1/2	1.39
B3	N6–b3–P*m*IA	20%P*m*IA	1/2	1.58
B4	N6–b1–PMA	10%PMA	1/2	1.15
B5	N6–b2–PMA	15%PMA	1/2	1.26
B6	N6–b3–PMA	20%PMA	1/2	1.44
B7	N6–b1–POA	10%POA	1/2	1.18
B8	N6–b2–POA	15%POA	1/2	1.32
B9	N6–b3–POA	20%POA	1/2	1.46

[a] N6: amine-terminated nylon-6 prepolymer ($\overline{M}_n \simeq 1000$).
B1–B9: multiblock copolyamides by the use of P-APA coupling agent.
[b] Measured at a concentration of 0.5 dl^{-1} in *N*MP + 5% LiCl at 30 °C.

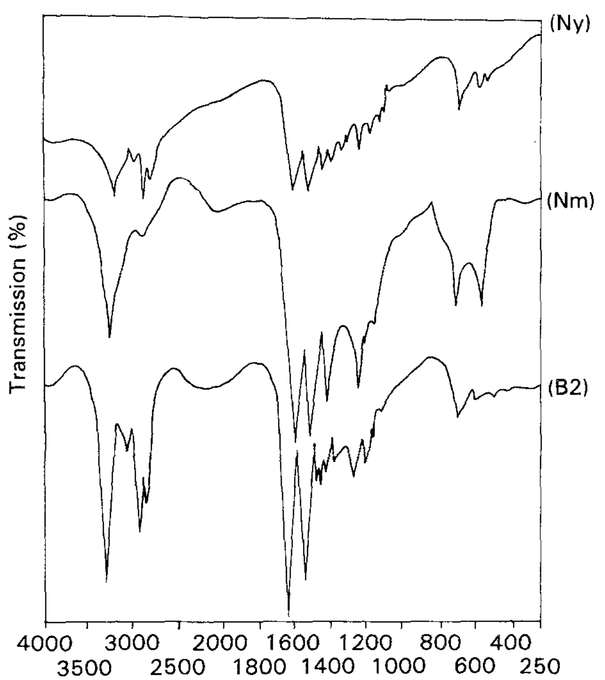


Figure 1 Infrared spectra of homopolymers and copolyamides of nylon-6–Nomex: (Ny), nylon-6 homopolymer; (Nm) Nomex homopolymer; (B2) multiblock copolyamides of Nomex 15 wt %.

TABLE III Characteristic absorptions of nylon-6 and aramid homopolymer

Characteristic absorptions	Polymers			
	Nylon-6	Nomex	PMA	POA
=N–H stretching vibration (cm^{-1})	3300	3400	3400	3400
=C=O (cm^{-1})	1650	1680	1660	1650
C$=\!=\!=$C (cm^{-1})	–	1540, 1610	1620, 1520	1510, 1620
–NHCO– on metasubstituted (cm^{-1})	1660	1450–1650	–	–
–NHCO– on parasubstituted (cm^{-1})	–	3000–3150	–	–
= N–H deformation (cm^{-1})	1560	1315–1550	–	–
–CH_2– stretching vibration (cm^{-1})	2990, 2770	–	2750–2950	–
–C_6H_4– on parasubstituted (cm^{-1})	–	–	800, 1100	–
–C_6H_4–CH_2–C_6H_4– (cm^{-1})	–	–	1530	–
–O– (cm^{-1})	–	–	–	1230

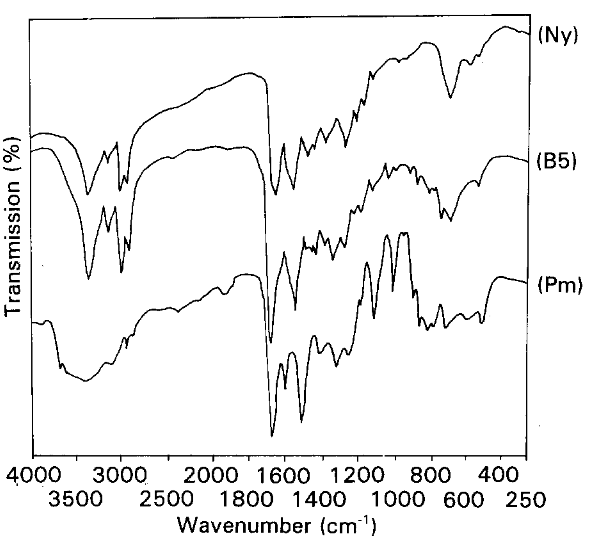


Figure 2 Infrared spectra of homopolymers and copolyamides of nylon-6–PMA: (Ny) nylon-6 homopolymer; (Pm) PMA homopolymer; (B5) multiblock copolyamides of PMA 15 wt %.

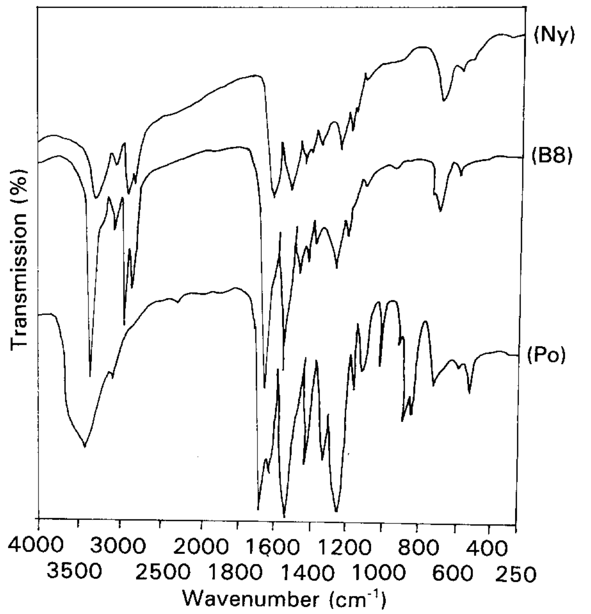


Figure 3 Infrared spectra of homopolymers and copolyamides of nylon-6–POA: (Ny) nylon-6 homopolymer; (Po) POA homopolymer; (B8) multiblock copolyamides of POA 15 wt %.

3.2. 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 semi-rigid and wholly-rigid aromatic polyamide (PMA, POA or Nomex) in nylon-6 is expected to produce better thermal properties. The thermal behaviour of the block copolymers and the blends which were measured by DSC [23, 24] is shown in Table IV, and Figs 4–6. From the results, it was shown that the glass transition temperature, T_g, of the polyblends increased with increasing aramid content. In particular, polyblends with the wholly-rigid Nomex could exhibit higher T_g than those of semi-rigid blends. This indicates that the mobility of nylon-6 chains is restrained in the amorphous region, the rotational motion of nylon-6, especially for wholly-rigid Nomex, could be larger than that of semi-rigid PMA or POA. It was also found that the glass transition temperature, T_g, and the melting point, T_m, of the block copolyamides increased significantly compared with that of the original nylon-6, and also exhibited higher values than those of the blends. Because the transition temperature

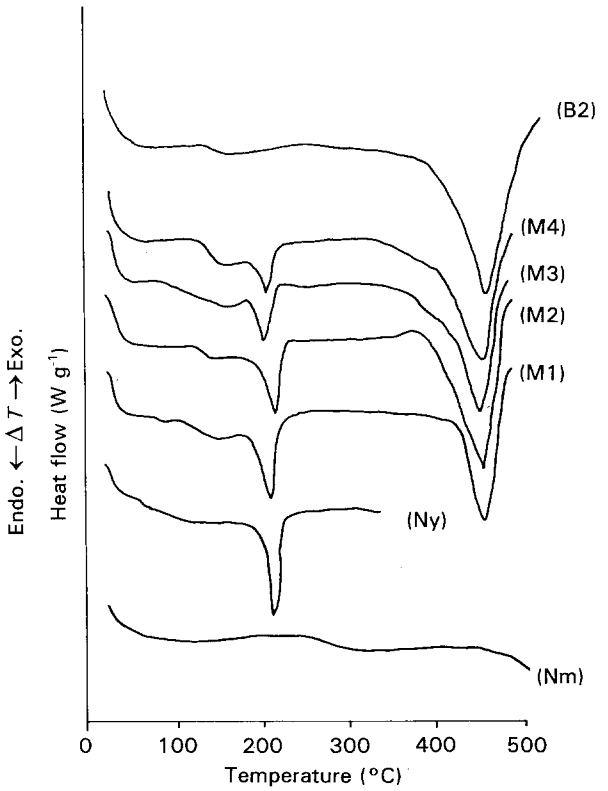


Figure 4 DSC plots of polyblends of nylon-6 with Nomex and nylon-6–Nomex block copolymers in nitrogen: (Nm) Nomex; (Ny) nylon-6; (M1) Nomex 5 wt %; (M2) Nomex 10 wt %; (M3) Nomex 15 wt%; (M4) Nomex 20 wt %; (B2) multiblock copolyamides of Nomex 15 wt%.

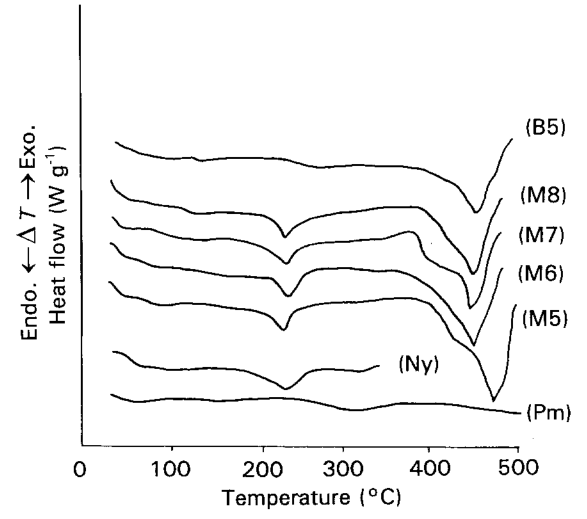


Figure 5 DSC plots of polyblends of nylon-6 with PMA and nylon-6–PMA block copolymers in nitrogen : (Pm) PMA; (Ny) nylon-6; (M5) PMA 5 wt %; (M6) PMA 10 wt%; (M7) PMA 15 wt %; (M8) PMA 20 wt %; (B5) multiblock copolyamide of PMA 15 wt%.

TABLE IV T_g, T_m and crystalline properties of nylon-6–aramid measured by DSC analysis

Code[a]	Polymer	T_g (°C)	T_m (°C)	X_c (%)[b]	ΔH_{fus} (J g^{-1})
Ny	Nylon-6	67	219	24	43
Pm	PMA 100%	300	> 500	–	–
Po	POA 100%	129	516	–	–
Nm	Nomex 100%	275	> 520	–	–
M1	Nomex 5%	130	218	38	71.8
M2	Nomex 10%	134	223	43	80.6
M3	Nomex 15%	139	216	40	75.5
M4	Nomex 20%	140	218	39	73.7
M5	PMA 5%	90	219	29	55.2
M6	PMA 10%	98	220	36	68.3
M7	PMA 15%	100	219	34	65.6
M8	PMA 20%	125	219	33	62.5
M9	POA 5%	82	218	25	47.5
M10	POA 10%	98	218	30	56.2
M11	POA 15%	101	219	33	62.6
M12	POA 20%	102	218	27	50.9
B2	N6-b2-Nomex 15%	140	454	–	–
B5	N6-b2-PMA 15%	135	448	–	–
B8	N6-b2-POA 15%	119	394	–	–

[a] Ny, Pm, Po, Nm: homopolymers of nylon-6, PMA, POA and Nomex. M1–M12: polyblends. B2, B5, B8: multiblock copolyamides of nylon-6–aramid.

[b] $X_c = \Delta H_\delta / \Delta H_f \times 100\%$ according to the literature [18, 19].

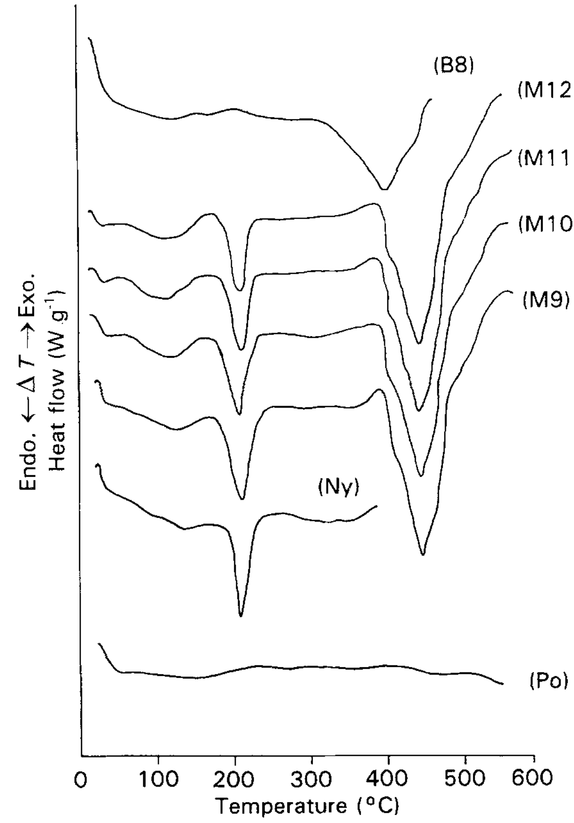


Figure 6 DSC plots of polyblends of nylon-6 with POA and nylon-6–POA block copolymers in nitrogen: (Po) POA; (Ny) nylon-6; (M9) POA 5 wt %; (M10) POA 10 wt %; (M11) POA 15 wt %; (M12) POA 20 wt %; (B8) multiblock copolyamides of POA 15 wt %.

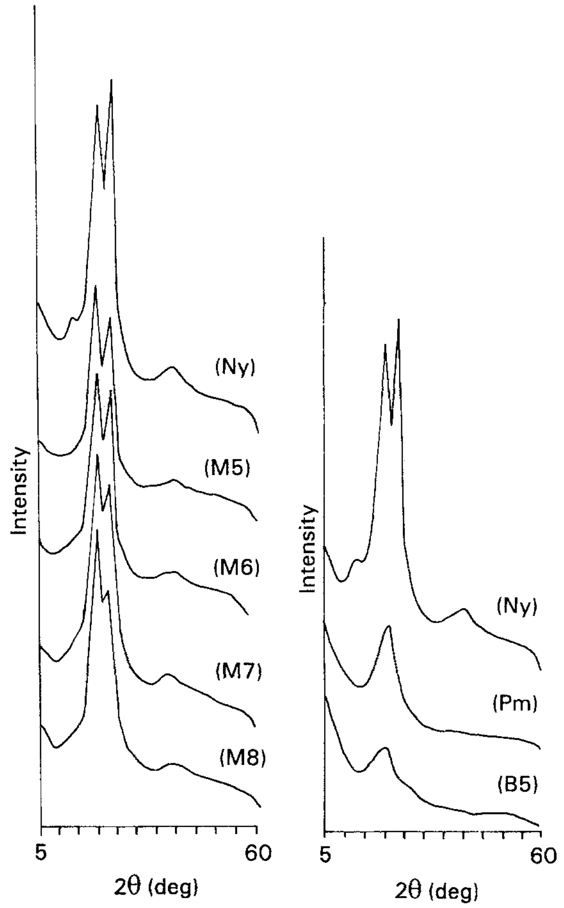


Figure 7 WAXD patterns of polyblends of nylon-6 with PMA and nylon-6–PMA block copolymers: (Ny) nylon-6 homopolymer; (Pm) PMA; (M5) PMA 5 wt%; (M6) PMA 10 wt %; (M7) PMA 15 wt %; (M8) PMA 20 wt %; (B5) multiblock copolyamides of PMA 15 wt %

could indicate the behaviour of molecular motion within the polymer, it could be used as a clue to identify their phase separation, or their compatibility [20].

The glass transition temperature, T_g, of block copolyamides showed only one peak; therefore, a compatible state of semi-rigid and wholly-rigid aramids with nylon-6 could be possible in the multiblock copolymer. From the DSC results it was revealed that the melting temperature, T_m, of the multiblock copolymers of both semi-rigid and wholly-rigid polyamides, was up to 400 °C. However, the T_m of the wholly-rigid Nomex copolyamide was higher than that of semi-rigid PMA or POA copolyamides. This might be due to the nylon-6 prepolymers and semi-rigid PMA or POA having the same monoclinic crystal structure [12–17]. Noticeably, the homopolymer of P*m*IA (Nomex) having the triclinic structure [18, 19], and its copolyamide, also exhibited better T_g and T_m, because the nylon-6–Nomex multiblock copolyamide had formed a new crystal structure. Both semi-rigid and wholly-rigid chain molecules have the same results, such as enhancing the T_g and T_m. On the contrary, the T_m of the polymer blends did not change much as the amounts of aramid were increased, remaining at about 220 °C. In general, the thermal properties of block copolymers were superior to those of polyblends.

3.3. Wide-angle X-ray diffraction

The wide-angle X-ray diffraction patterns of nylon-6 homopolymer and polyblends, and block copolymer

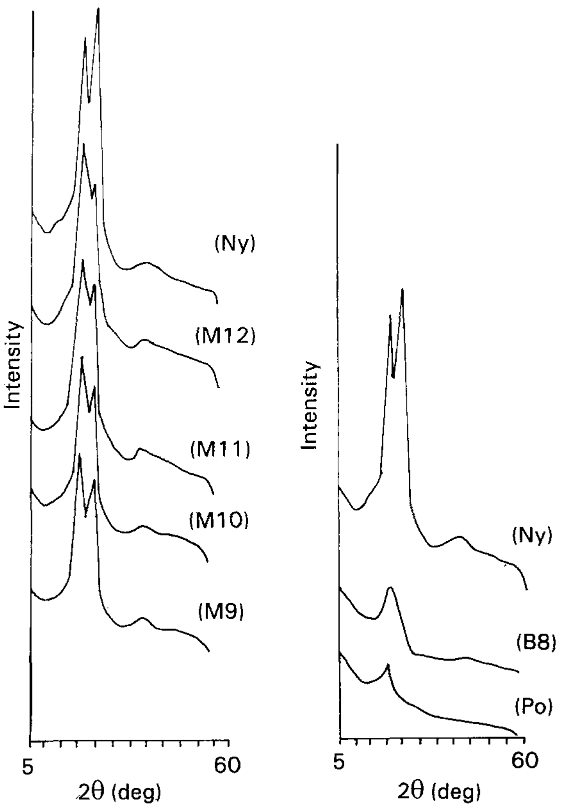


Figure 8 WAXD patterns of polyblends nylon-6 with POA and nylon-6–POA block copolymers: (Ny) nylon-6 homopolymer; (Po) POA; (M9) POA 5 wt%; (M10) POA 10 wt %; (M11) POA 15 wt %; (M12) POA 20 wt %; (B8) multiblock copolyamides of POA 15 wt %

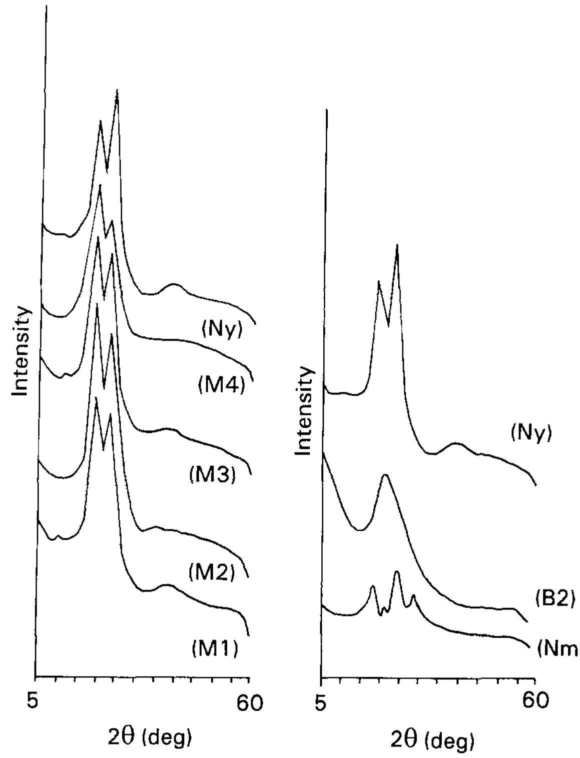


Figure 9 WAXD patterns of polyblends of nylon-6 with Nomex and nylon-6–Nomex block copolymers: (Ny) nylon-6 homopolymer; (Nm) Nomex; (M1) Nomex 5 wt %; (M2) Nomex 10 wt %; (M3) Nomex 15 wt %; (M4) Nomex 20 wt %; (B2) multiblock co-polyamides of Nomex 15 wt %.

TABLE V *d*-spacing, crystallite size, and degree of crystallinity of nylon-6–aramid polyblends and copolyaramides

Code[a]	Polymer	*d* (200) (nm)	*d* (002,202) (nm)	*L* (200) (nm)	*L* (002,202) (nm)	X_c (%)
Ny	Nylon-6	0.4373	0.3719	13.2	12.5	30
M1	P*m*IA 5%	0.4373	0.3719	13.2	11.7	36
M2	P*m*IA 10%	0.4373	0.3719	13.2	11.0	39
M3	P*m*IA 15%	0.4372	0.3719	13.4	10.9	37
M4	P*m*IA 20%	0.4372	0.3719	13.4	10.7	35
M5	PMA 5%	0.4373	0.370	13.3	12.4	35
M6	PMA 10%	0.4373	0.370	13.5	12.0	39
M7	PMA 15%	0.4385	0.370	13.2	11.7	38
M8	PMA 20%	0.4382	0.370	13.4	11.0	37
M9	POA 5%	0.4369	0.3721	13.2	11.9	34
M10	POA 10%	0.4373	0.3721	13.0	11.3	36
M11	POA 15%	0.4369	0.3721	12.9	10.9	38
M12	POA 20%	0.4373	0.3721	13.1	10.7	37
B2	N6-b2-P*m*IA 15%	0.4365	–	11.0	–	–
B5	N6-b2-PMA 15%	0.433	–	12.0	–	–
B8	N6-b2-POA 15%	0.435	–	12.1	–	–

[a] Ny: homopolymer of nylon-6. M1–M12: polyblends of nylon-6–aramid. B2, B5, B8: multiblock copolyamides of nylon-6–aramid.

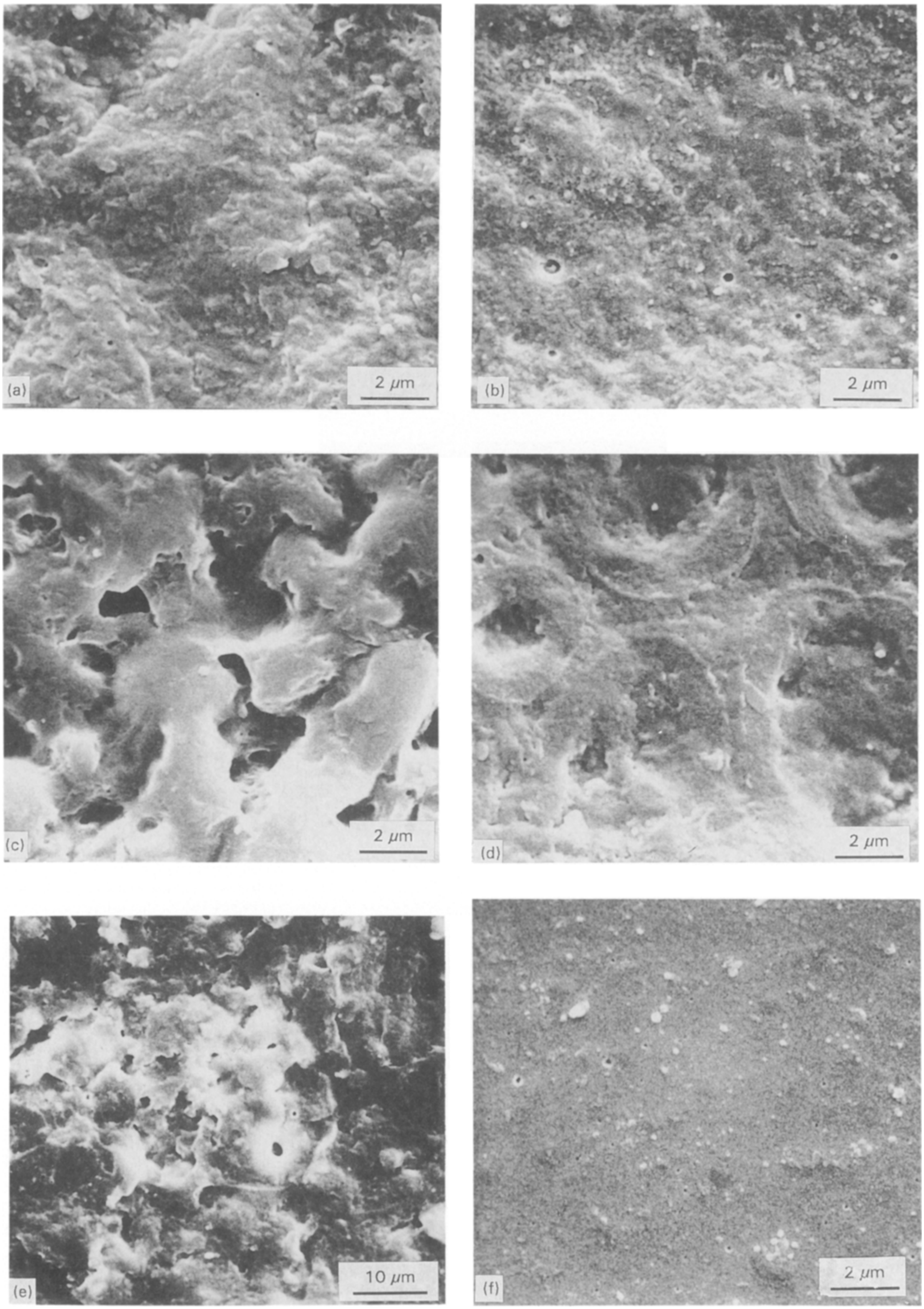


Figure 10 Scanning electron micrographs of nylon-6–Nomex polyblends, and block copolyamide: (a) blend of nylon-6 with Nomex 5 wt %; (b) Nomex 10 wt %; (c) Nomex 3 wt %, after extraction of nylon-6 from the blend with HCOOH; (d) Nomex 3 wt %, after extraction of Nomex from the blend with DMAc; (e) Nomex 15 wt %, after extraction of nylon-6 from the blend with HCOOH; (f) multiblock copolyamide with Nomex of 15 wt%.

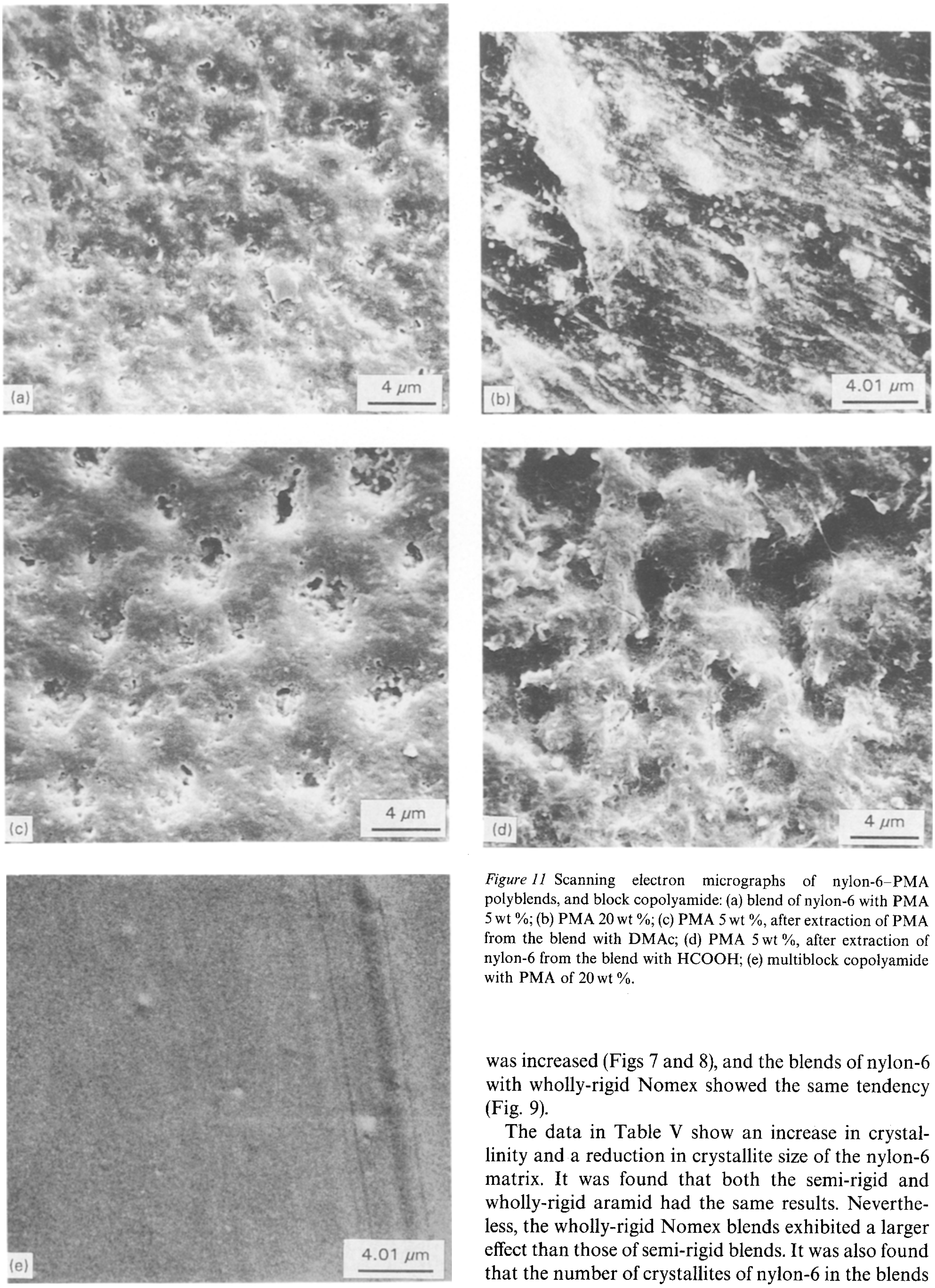
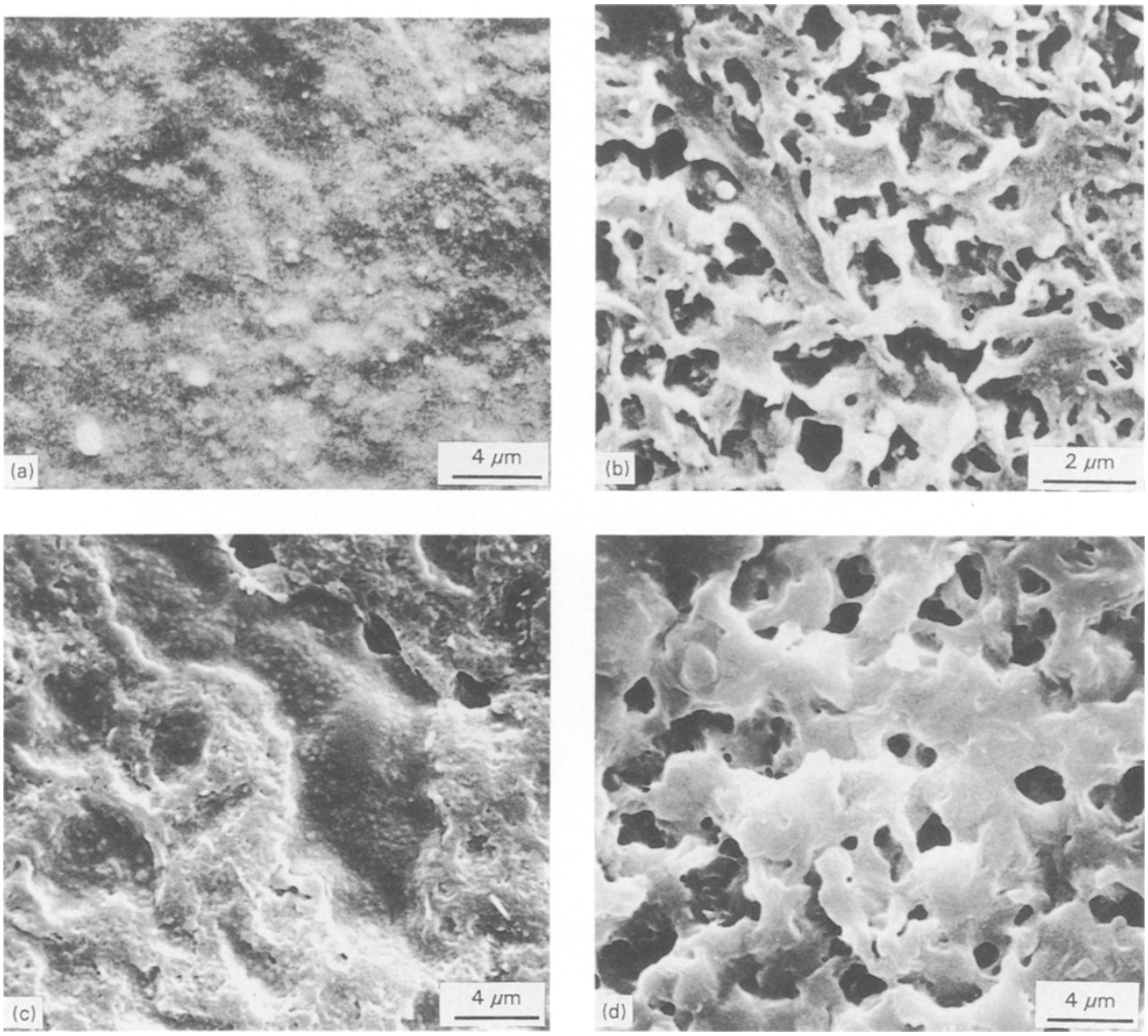


Figure 11 Scanning electron micrographs of nylon-6–PMA polyblends, and block copolyamide: (a) blend of nylon-6 with PMA 5 wt %; (b) PMA 20 wt %; (c) PMA 5 wt %, after extraction of PMA from the blend with DMAc; (d) PMA 5 wt %, after extraction of nylon-6 from the blend with HCOOH; (e) multiblock copolyamide with PMA of 20 wt %.

were measured using a Rigaku diffractometer. From the X-ray diffraction results, blends of nylon-6 with semi-rigid aromatic polyamide PMA, POA or PSA [6, 7] had crystallite sizes of nylon-6 which apparently became smaller as the amount of semi-rigid aramid was increased (Figs 7 and 8), and the blends of nylon-6 with wholly-rigid Nomex showed the same tendency (Fig. 9).

The data in Table V show an increase in crystallinity and a reduction in crystallite size of the nylon-6 matrix. It was found that both the semi-rigid and wholly-rigid aramid had the same results. Nevertheless, the wholly-rigid Nomex blends exhibited a larger effect than those of semi-rigid blends. It was also found that the number of crystallites of nylon-6 in the blends gradually increased with increasing aramid contents, being consistent with the morphological structure seen by scanning electron microscopy (SEM) observations. However, it should be noted that the crystallite size in the α (0 0 2, 2 0 2) plane became smaller, but that in the α (2 0 0) plane did not, as more semi-rigid or wholly-rigid aromatic polyamide was present. Noticeably, the crystallite size in the α (0 0 2, 2 0 2) plane of wholly-rigid



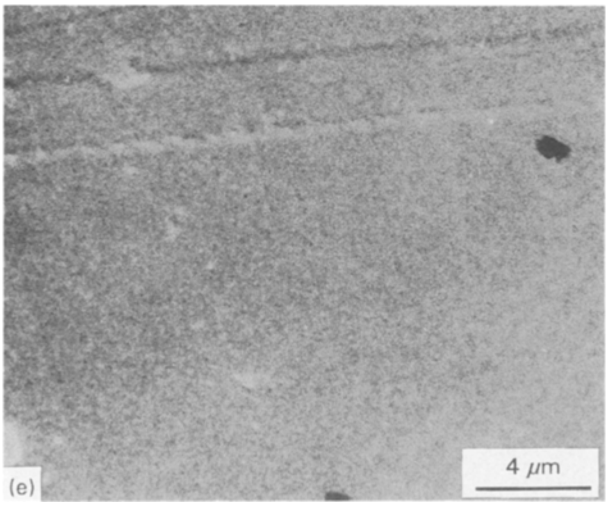


Figure 12 Scanning electron micrographs of nylon-6–POA polyblends, and block copolyamide: (a) blend of nylon-6 with POA 3 wt %; (b) POA 5 wt %, after extraction of POA from the blend with DMAc; (c) POA 20 wt %, after extraction of POA from the blend with DMAc; (d) POA 20 wt %, after extraction of nylon-6 from the blend with HCOOH; (e) multiblock copolyamide with POA of 20 wt %.

Nomex-reinforced nylon-6 blends had a smaller value than that of semi-rigid PMA- or POA-reinforced nylon-6 blends. In addition, the *d*-spacing remained almost constant. Thus, it could be concluded that the greater the content of the blended aromatic polyamide the more the crystal growth of the nylon-6 chain in the α(0 0 2, 2 0 2) plane could be retarded. In addition, the effect of the wholly-rigid chain Nomex on the nylon-6 matrix was higher than that of semi-rigid chain PMA or POA. From the wide-angle X-ray diffraction pattern, it was found that the semi-rigid and wholly-rigid aramid-reinforced nylon-6 blends all exhibited two diffraction peaks, ie. $2\theta = 20.5°$ and $24°$. However, the multiblock copolyamides had only peak at $2\theta = 20°$ (Figs 7–9), indicating a different crystal structure of multiblock copolyamides. Thus, this might be attributable to the same monoclinic crystal structure of nylon-6 and semi-rigid PMA or POA. However, the fact that the wholly-rigid Nomex of triclinic crystal structure gave the same result, i.e. the (2 0 0) plane of nylon-6–Nomex multicopolyamide in a structure of nylon-6, indicated it had formed a new crystal structure.

3.4. Morphological observation

The scanning electron microscope was used to visualize the microstructure of the polyblends and copolymers. It is seen in Fig. 10 that although the nylon-6 homopolymer appeared to have a uniform surface structure, its polyblends showed dispersed phase structures in both semi-rigid and wholly-rigid aramid-reinforced polymer blends (Figs 10–12). From observation of the scanning electron micrographs, it was seen that the semi-rigid and wholly rigid PMA, POA and Nomex were aggregated in grain particles between the nylon-6 matrix. By treating the polyblend films with DMAc or formic acid, we could distinguish between the nylon-6 continuous parts and the aromatic polyamide aggregated parts (Figs 10c–e, 11c and d, 12c and d). Nevertheless, it was found that multiblock copolyamides exhibited a more homogeneous structure than those of the polyblends (Figs 10f, 11e, and 12e).

3.5. Mechanical properties of polyblends and block copolymers

Mechanical properties of polyblends and block copolymers are presented in Table VI and Figs 13–15.

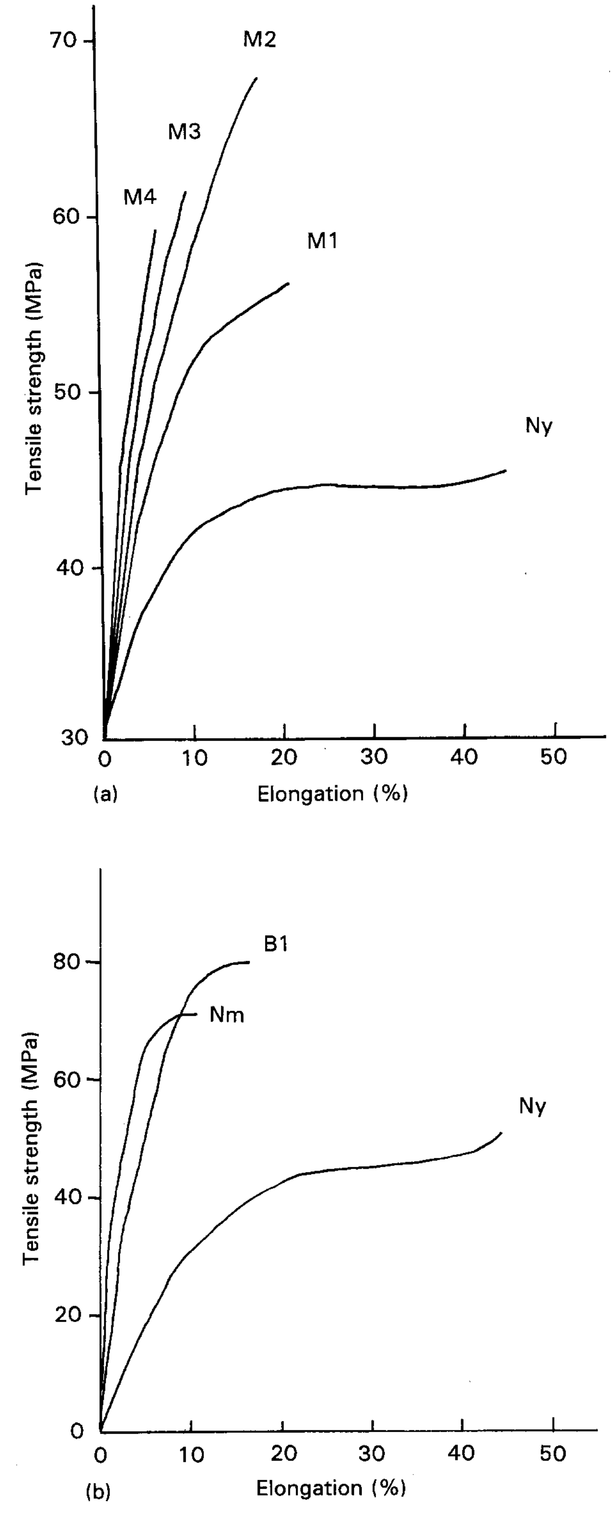


Figure 13 Stress–strain curves of nylon-6–Nomex polyblends, and block copolyamide: (Ny) nylon-6 homopolymer; (Nm) Nomex; (M1) Nomex 5 wt %; (M2) Nomex 10 wt %; (M3) Nomex 15 wt %; (M4) Nomex 20 wt %; (B1), multiblock copolyamides of Nomex 10 wt %.

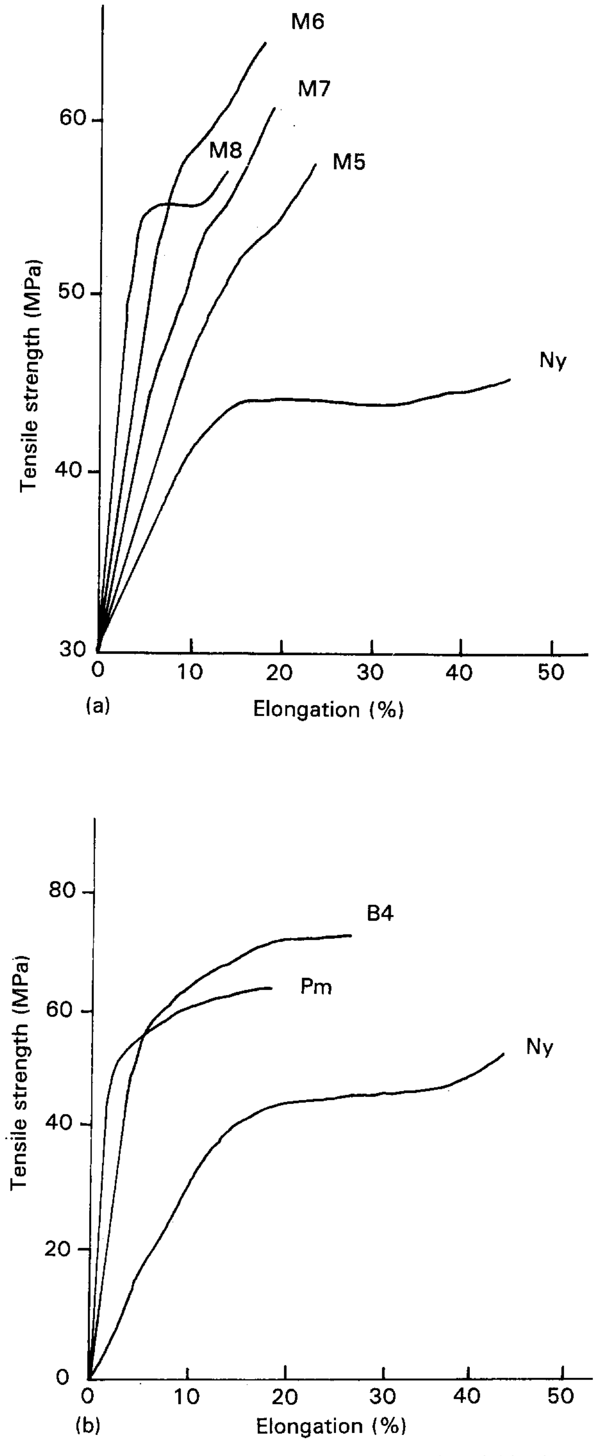


Figure 14 Stress–strain curves of nylon-6–PMA polyblends, and block copolyamide: (Ny) nylon-6 homopolymer; (Pm) PMA; (M5) PMA 5 wt %; (M6) PMA 10 wt %; (M7) PMA 15 wt %; (M8) PMA 20 wt %; (B4) multiblock copolyamides of PMA 10 wt %.

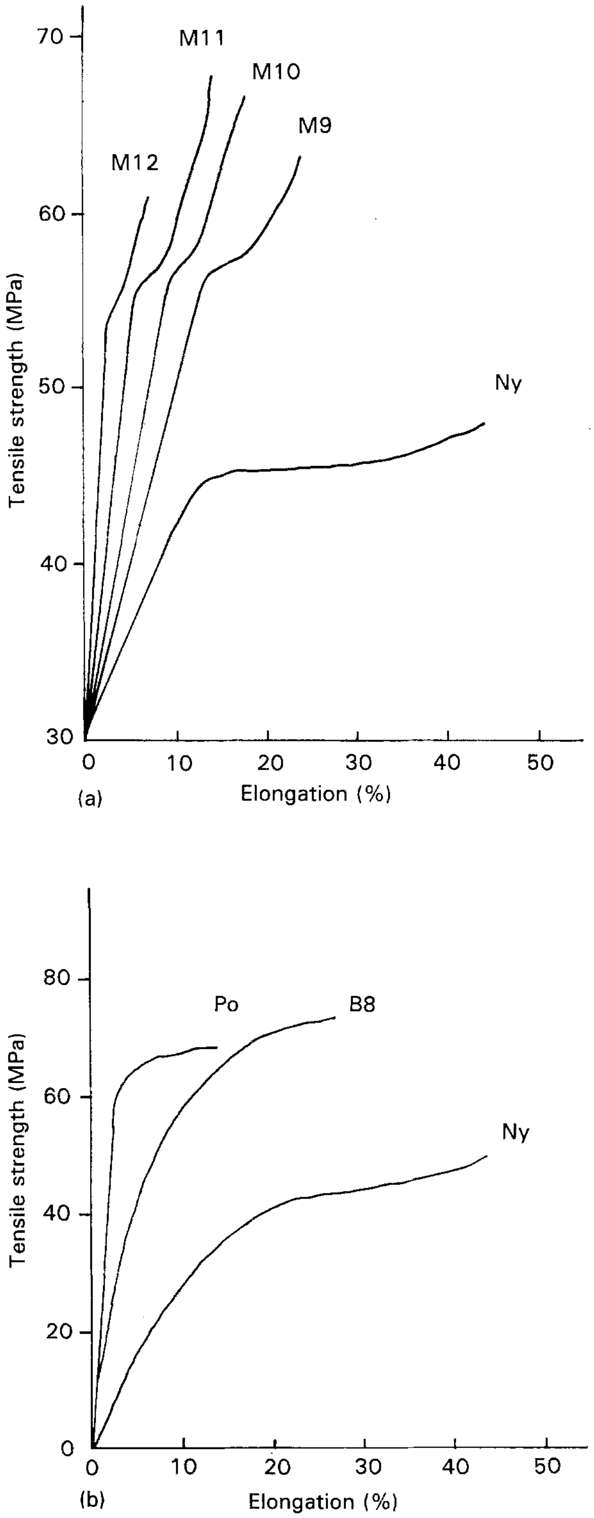


Figure 15 Stress–strain curves of nylon-6–POA polyblends, and block copolyamide: (Ny) nylon-6 homopolymer; (Po) POA; (M9) POA 5 wt %; (M10) POA 10 wt %; (M 11) POA 15 wt %; (M12) POA 20 wt %; (B8) multiblock copolyamides of POA 15 wt %.

TABLE VI Mechanical properties of nylon-6–aramid polyblends, and copolyamides

Code[a]	Polymer	T_b (MPa)[b]	E_b (%)	M_i (GPa)[b]
Ny	Nylon-6	45.19	44	0.886
Pm	PMA	64.02	17	7.204
Po	POA	68.15	14	8.023
Nm	Nomex	70.08	11.2	9.260
M1	Nomex 5%	55.42	21.2	1.41
M2	Nomex 10%	63.85	13.7	1.58
M3	Nomex 15%	60.73	8.5	1.63
M4	Nomex 20%	59.02	5.9	1.67
M5	PMA 5%	57.63	21.9	1.393
M6	PMA 10%	63.73	17.8	1.421
M7	PMA 15%	60.34	17.7	1.458
M8	PMA 20%	56.05	13.8	1.630
M9	POA 5%	63.31	21	1.393
M10	POA 10%	66.67	18	1.467
M11	POA 15%	68.32	14	1.550
M12	POA 20%	61.91	9	1.718
B1	N6-b1-Nomex 10%	78.93	15.6	8.980
B4	N6-b2-PMA 15%	69.06	27	5.364
B8	N6-b2-POA 15%	72.33	26	5.843

[a] Ny, Pm, Po, Nm: homopolymer of nylon-6, PMA, POA and Nomex. M1–M12: polyblends of nylon-6 with aramid. B1, B4, B8: multiblock copolyamides of nylon-6–aramid.

[b] T_b, E_b, M_i: breaking tensile strength, elongation, initial modulus.

For polyblends (M1–M12) (Figs 13a, 14a, and 15a), it was found that the tensile strength, T_b, and the initial modulus, M_i, were progressively increased as the content of aromatic polyamide was increased. This trend may result from the immobility and rigidity of the aggregated aromatic polyamide domain and also the increase of tie molecules connecting intercrystalline or intracrystalline regions between the nylon-6 polymer chains [25, 26]. On the other hand, the plastic deformation of the blends was reduced, due to the restraint of the semi-rigid PMA, POA molecules and wholly-rigid Nomex molecules, so that the yield strength was enhanced, but the ultimate elongation decreased. It was very noticeable that the wholly-rigid Nomex reinforced nylon-6 blends (M1–M4) exhibited higher mechanical properties than those of semi-rigid PMA- or POA-reinforced nylon-6. Moreover, it was observed that the blends containing more than 10 wt% PMA or 15 wt% POA semi-rigid molecules and/or 10 wt% Nomex wholly-rigid molecules, exhibited a reduction of mechanical properties. The tensile strength of multiblock copolyamides appeared to be higher than that of polyblends, and the wholly-rigid Nomex reinforced block copolyamides exhibited higher values than those of semi-rigid reinforced block copolyamides (Figs 13b, 14b and 15b).

4. Conclusions

Twelve nylon-6/Aramid polyblends were prepared by physical blending and nine nylon-6–Aramid multiblock copolyamides were synthesized by chemical extension using P-APA as a coupling agent. The reinforcement of nylon-6 with semi-rigid PMA, POA and wholly-rigid P*m*IA (Nomex) proved to be successful. Block copolymers showed, for the same content of aromatic polyamide, better mechanical properties than those of polyblends. Nevertheless, comparisons of the semi-rigid aromatic polyamide-reinforced nylon-6 polyblends and block copolyamides with those of the wholly-rigid aromatic polyamide reinforced, showed that the wholly-rigid sample exhibited higher mechanical properties than those of the semi-rigid sample.

The morphological features demonstrated that the disperse-phase structure was present in polyblends, although the copolyamides exhibited a more homogeneous, compatible structure.

From DSC analysis, it was found that both the semi-rigid and wholly-rigid aramid-reinforced nylon-6 polyblends exhibited a higher glass transition temperature, T_g, than that of nylon-6 homopolymer, which increased with increasing aramid content. The T_g and T_m of block copolyamides were even higher than those of the polyblends. Noticeably, the wholly-rigid chain-reinforced nylon-6 polyblends and block copolyamides exhibited better thermal properties than those of the semi-rigid chain samples. X-ray diffraction analysis found that the polyblends and nylon-6 homopolymer had two diffraction peaks, i.e. $2\theta = 20.5°$ and 24°. However, the multiblock copolyamides had only one peak at $2\theta = 20°$, indicating the different crystal structure of the multiblock copolyamides. In addition, the data exhibited an increase in crystallinity and a reduction in crystallite size in the α (0 0 2, 2 0 2) plane of the nylon-6 matrix, which gradually increased with increasing aramid contents.

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