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The block copolymer of nylon-6 with semi-rigid poly(p-diphenylmethyl terephthalamide)

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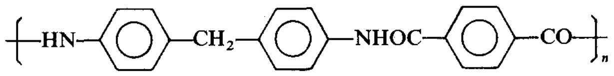
In this study, the flexible nylon-6 was reinforced by the semi-rigid aromatic polyamide poly(p-diphenylmethyl terephthalamide) through chemical copolymerization using p-aminophenylacetic acid as a coupling agent. From differential scanning calorimetry it was discovered that the T_g and T_m of multiblock copolyamides were higher than those of triblock copolyamides. From observation by scanning electron microscopy the multiblock copolyamides exhibited a homogeneous texture rather than an aggregated one. We found that in wide-angle X-ray diffraction patterns the triblock copolyamides had two diffraction peaks, i.e. $2\theta = 20$ and $24°$. However, the multiblock had only one peak 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 triblock copolyamides.

1. Introduction

Recently, a number of attempts have been made to improve the mechanical properties of aliphatic nylons through the physical blending and chemical modification of aromatic polyamides such as Kevlar, polybenzamide (PBA) [1–5] or poly (4,4-diphyenyl sulphone terephthalamide) (PSA) [6–9]. As shown in our previous papers [6–12], aliphatic nylon-6 which is modified by the semi-rigid PSA or wholly rigid Nomex did exhibit better thermal and mechanical properties. In this study we used the semi-rigid polyamide poly(p-diphenylmethyl terephthalamide) (PMA) to reinforce the aliphatic nylon-6. The chemical structure of PMA is as follows:



Scheme 1

The semi-rigid PMA has the same monoclinic crystal structure [13–18] as that of nylon-6.

2. Experimental procedure

2.1. Materials

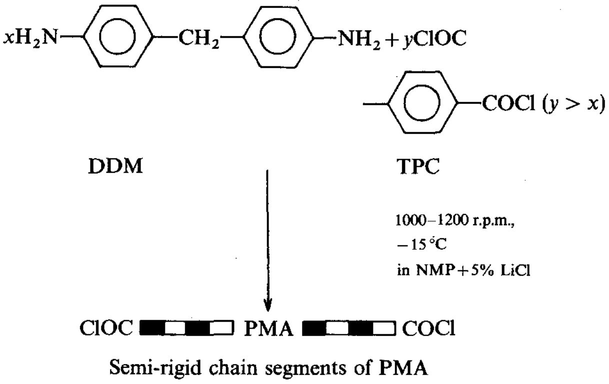
Nylon-6 was obtained from the Formosa Chemical and Fiber Corporation. The sample was first dissolved in formic acid and then poured into a large amount of water. Samples were refluxed with methanol and hot water for 16 h and after that dried at 100 °C under vacuum for 8 h. The inherent viscosity ($\eta_{inh} = 1.24$) and $\bar{M}_n$ (21,500) were obtained from the literature [19].

Terephthaloyl dichloride (TPC), 4,4′-diaminodiphenyl methane (DDM) and 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 and 14 mm Hg 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 was dried under vacuum at 160 °C for 5 h.

2.2. Preparation of polyamides and their prepolymers

Low molecular weight semi-rigid PMA prepolymer was prepared from excess TPC with DDM in NMP containing 5% LiCl at − 15 °C for 30 min [8–12]. The reaction scheme was as follows:



Scheme 2

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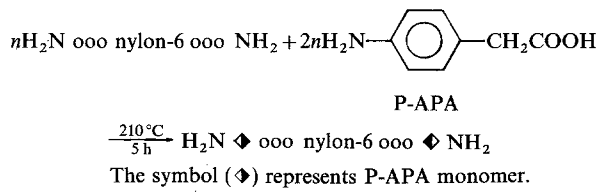
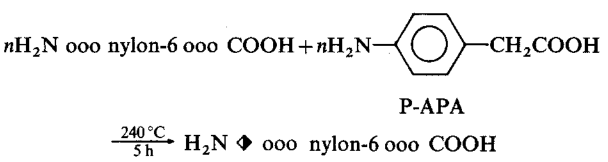
A low molecular weight diamine-terminated nylon-6 prepolymer was prepared with an excess of hexamethylene diamine (HMDA) as described in the literature [20,21]. The prepolymer was reacted with P-APA coupling agent at 210 °C for 5 h as follows:



The symbol (◆) represents P-APA monomer.

Scheme 3

The product was purified and dissolved in NMP + 5% LiCl solution for further use. Long-chain monoamine-terminated nylon-6 prepolymer was also prepared by bulk polymerization at 240 °C for 5 h as follows:



Scheme 4

The characteristics of all the syntheses are given in Table I. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were determined with a Waters gel permeation chromatograph. The solvent was N,N-dimethylformamide containing 0.05 M LiCl and the column was μ.Bondagel E-Linear, calibrated at a flow rate of 1 ml min^{-1}.

2.3. Synthesis of nylon-6–PMA block copolymers

The copolyamides were synthesized by reacting 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 (bath A) and the aramid PMA prepolymer ($\bar{M}_n = 1180$) also in NMP + 5% LiCl (bath B) were allowed to mix and were stirred vigorously in an N$_2$ atmosphere at − 5–10 °C for 30 min and then raised to room temperature, being 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.

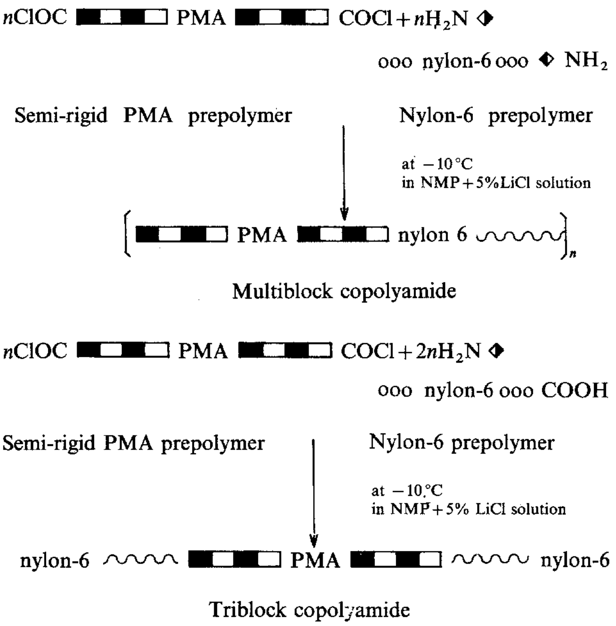
TABLE I Characteristics of prepolyamides and PMA

Prepolymer[a]	N6	N6$_a$	PMA
M_n[b]	998	1300	1180

[a] N6: amine-terminated nylon-6 (by HMDA). N6$_a$: aromatic diamine-terminated nylon-6 (by P-APA). Elemental analysis (%): C(64.2), H(9.6), N(12.5).

[b] $\bar{M}_n = 15\,600\ \eta_{inh}^{1.49}$ according to the literature [16].

Noticeably, all the copolyamides obtained here were dissolved in the NMP + 5% LiCl solution, but they were not soluble in formic acid of m-cresol, although these were good solvents for nylon-6. The detailed reaction schemes are as follows:



Scheme 5

The various multiblock and triblock copolyamides were prepared by low-temperature polymerization of nylon-6 prepolymer with various amounts (wt%) of semi-rigid 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 sufficiently higher molecular weight. In general, the chain-extending reaction could be completed in 10–15 min and could yield as high a molecular weight copolymer as those of nylon-6–PSA copolyamides in our previous paper [6–9]. All the nylon-6–PMA copolyamides are summarized in Table II.

2.4. Measurements

Infarared spectra of homopolymers and copolymers were obtained (Hitachi Model 260–50) over the range

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	–	1.78

[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 ($\bar{M}_n = 1000$). 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.

400–4000 $\mathrm{cm^{-1}}$. The samples were in the form of a film of about 10 μm thickness.

Elemental analysis (C, H and N) was performed by a 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 Du Pont model 9900 DSC, with a heating rate of 20 °C $\mathrm{min^{-1}}$ to obtain the glass temperature (T_g) and the melting temperature (T_m).

Wide-angle X-ray spectroscopy (WAXS) photographs were taken with Ni-filtered CuK_α radiation using a Rigaku D/max-II X-ray diffractometer.

A scanning electron microscope (Cambridge Stereoscan-600) was also used to observe the morphological structure of samples that were sputter-coated with Au to prevent their oxidation.

All stress–strain data was obtained on an Instron 1122 testing instrument at an extension rate of 5 mm $\mathrm{min^{-1}}$ and full load of 50 kg.

3. Results and discussion

3.1. Infrared spectra

The transmission infrared spectra of homopolymers and block copolymers are shown in Fig. 1. The infrared spectrum of nylon-6 (curve N_y) was characterized by 3300 $\mathrm{cm^{-1}}$ (=N–H stretch vibration), 1650 $\mathrm{cm^{-1}}$ (=C=O), 1560 $\mathrm{cm^{-1}}$ (=NH deformation), and 2900 and 2770 $\mathrm{cm^{-1}}$ ($-CH_2-$ stretch vibration) absorptions.

The infrared spectrum of PMA (curve Pm) was characterized by 1530 $\mathrm{m^{-1}}$ ($-C_6H_4-CH_2-C_6H_4-$), 1660 $\mathrm{cm^{-1}}$ (-CONH-), and 1100 and 800 $\mathrm{cm^{-1}}$ ($-C_6H_4-$ parasubstituted) absorptions.

The nylon-6–PMA block copolymers (curve B_{M1}) showed the characteristic absorptions of both nylon-6 and PMA. Noticeable was a characteristic absorption of the aliphatic $-CH_2-$ at 2900, 2770 $\mathrm{cm^{-1}}$ and at 1530 $\mathrm{cm^{-1}}$ ($-C_6H_4-CH_2-C_6H_4$) for the block copolymers with P-APA as a coupling agent. This came from the reaction of the $-NH_2$ on the paraposition of benzene with the paraposition -COCl group of the PMA prepolymer.

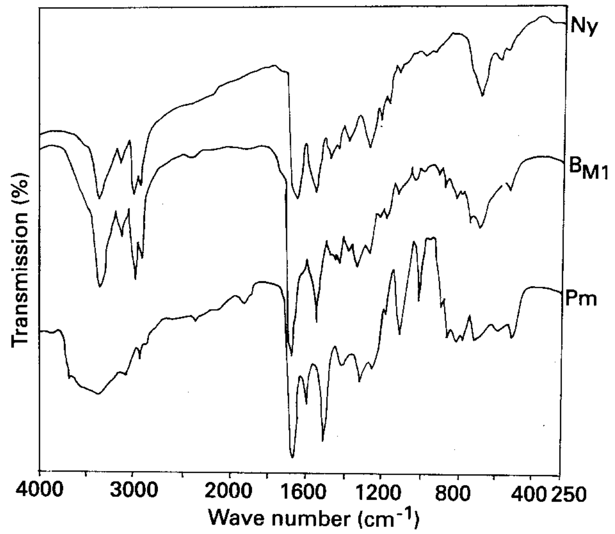


Figure 1 Infrared spectra of homo- and copolyamide films: (N_y) nylon-6 homopolymer, (P_m) PMA homopolymer, (B_{M1}) multiblock copolyamide of PMA (10 wt %).

3.2. Thermal properties

Polymer with an aromatic ring structure could contribute to thermal stability. Through this study, the presence of aromatic PMA in nylon-6 could be expected to provide better thermal properties. The thermal behaviour of homopolymers and block copolymer as measured by DSC is shown in Fig. 2 and Table III.

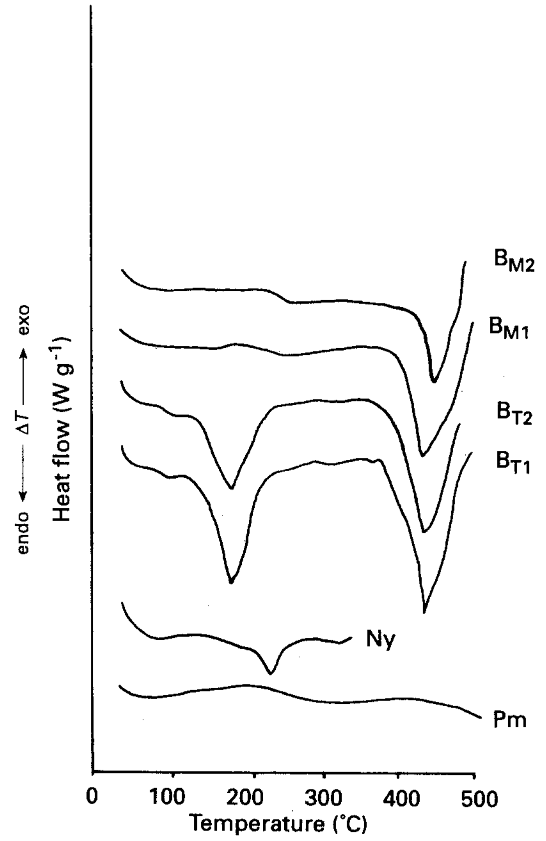


Figure 2 DSC plots of nylon-6–PMA block copolymers in nitrogen: (P_m) PMA, (N_y) nylon 6, (B_{T1}) triblock copolyamide of 10 wt % PMA content, (B_{M1}) multiblock copolyamide of 10 wt % PMA content, (B_{T2}) triblock copdynamide of 20 wt % PMA content, (B_{M2}) multiblock copolyamide of 20 wt % PMA content.

TABLE III T_g, T_m measured by DSC analysis

Code	Polymer	T_g(°C)	T_m(°C)
Ny	Nylon 6	67	219
Pm	PMA	300	> 510
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 copolyamides (PMA contents 10 and 20 wt %).
[b] B_{M1}, B_{M2}: multiblocks copolyamide (PMA contents 10 and 20 wt %).

It is also shown in Fig. 2 and Table III that the glass transition temperature (T_g) and the melting point (T_m) of the block copolyamides were increased significantly compared with that of the original nylon-6. Since the transition temperature could indicate the behaviour of molecular motion within the polymer, it could be used as a clue to identify the separation of phases or their compatibility [22]. The T_g of multiblock copolyamides shows only one peak; therefore, a compatible state of semi-rigid PMA with nylon-6 could be possible in the multiblock copolymer. From the results of DSC analysis, it is found that the melting temperature of the multiblock copolyamides was up to 400 °C. Their block copolyamides also exhibited higher T_g and T_m because the nylon-6–PMA multiblock copolyamide has formed a new crystal structure.

3.3. Wide-angle X-ray scattering

From the WAXS diffraction pattern (Figs 3 and 4 and Table IV) it was found that the nylon-6–PMA triblock copolyamides (B_{T1}, B_{T2}) all had two diffraction peaks, i.e. $2\theta = 20$ and 24° as did nylon-6. However, the multiblock copolyamides had only one at $2\theta = 20°$, evidently indicating the formation of a new crystal structure of multiblock copolyamides, i.e. the (2 0 0) plane of nylon-6–PMA multiblock copolyamide in a structure of nylon-6 had formed a new crystal structure.

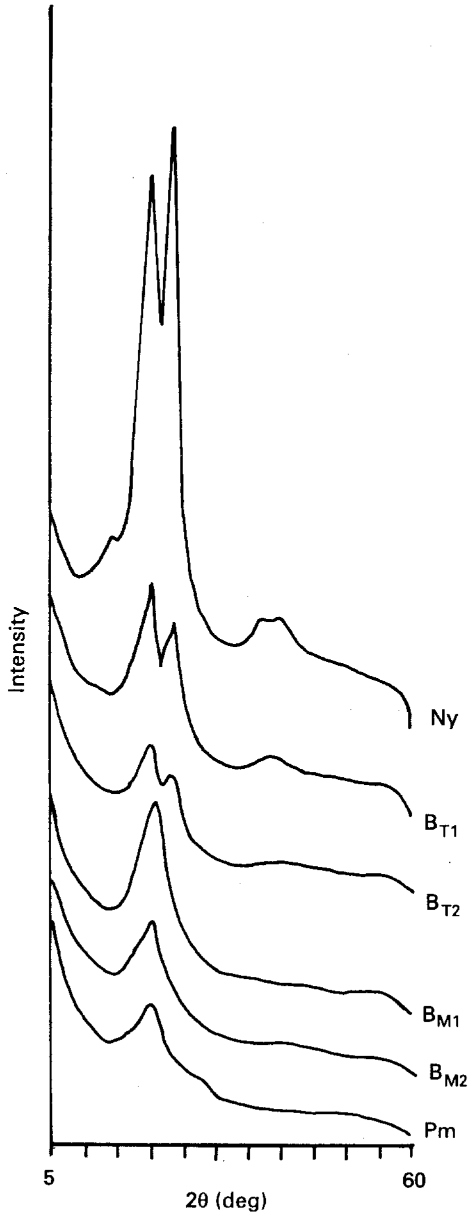


Figure 3 X-ray diagrams of homopolymers and block copolyamides: (N_y) nylon-6 100%, (P_m) PMA 100%, (B_{T1}, B_{T2}) triblock copolyamides of 10 and 20 wt % PMA content, (B_{M1}, B_{M2}) multiblock copolyamides of 10 and 20 wt % PMA content.

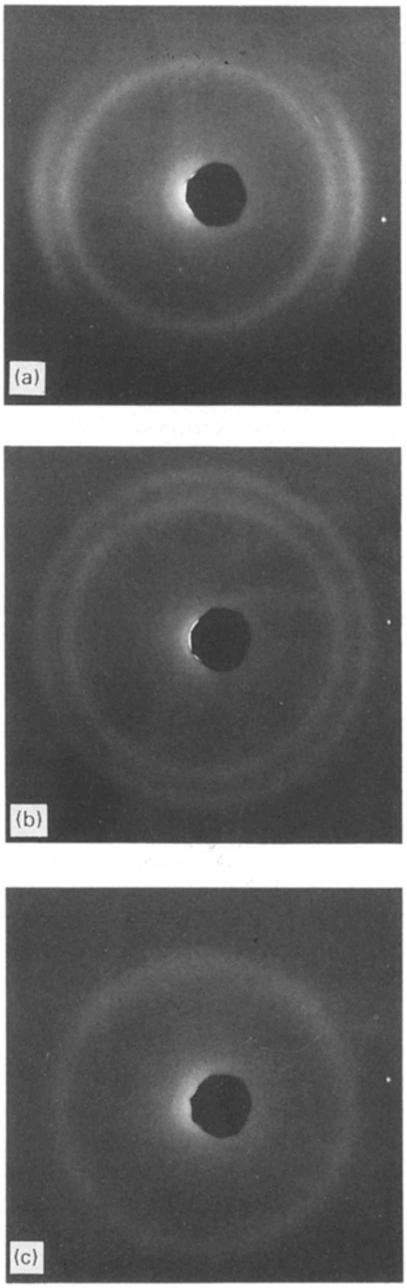


Figure 4 WAXS patterns of nylon-6 and block copolyamides: (a) (N_y) nylon-6 100%, (b) (B_{T1}) triblock copolyamides of 10 wt % PMA content, (c) (B_{M1}) multiblock copolyamides of 10 wt % PMA content.

3.4. Morphological observations

It was found from scanning electron microscopy (SEM) (Fig. 5) that the morphology of multiblock copolyamides exhibited a more homogeneous texture rather than an aggregated one [8], revealing that the triblock copolyamides had a dispersed phase structure.

TABLE IV Diffraction spacings and crystallite sizes of nylon-6–PMA block copolyamides

Code	Polymer	$d(200)$ (nm)	$d(002, 202)$ (nm)	$L(200)$ (nm)	$L(002, 202)$ (nm)
Ny	Nylon-6	0.4373	0.3719	13.2	12.5
B_{T1}[a]	Triblock 10%	0.4550	0.3780	–	–
B_{M1}[a]	Multiblock 10%	0.4330	–	12.0	–

[a] B_{T1}, B_{M1}: triblock and multiblock copolyamides (PMA content 10 wt %)

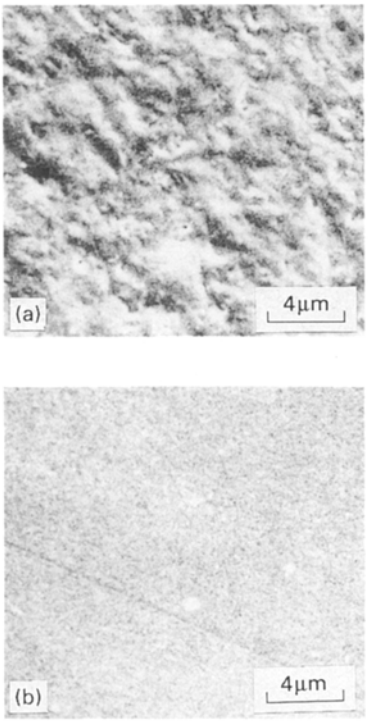


Figure 5 SEM photographs of (a) triblock and (b) multiblock copolyamides of 15 wt % PMA content.

3.5. Mechanical properties

The results on the mechanical performance after incorporating the PMA block segment in copolymers (B_{T1}, B_{M1}) are given in Table V and Fig. 6. It was found that the multiblock copolyamide prepared by using P-APA as a coupling agent had much better tensile strength and elongation than those of a polyblend [10] with the same amount (10 wt %) of PMA. Nevertheless, data for the triblock copolyamide still lay between nylon-6 and PMA homopolymer. The ordered block copolyamides has better properties, not only by the introduction of semi-rigid units which caused a higher intramolecular stiffness, but also by the increase of the intermolecular forces between polymer chains, and therefore formation of a more uniform and compatible structure.

TABLE V Mechanical properties of nylon-6–PMA block copolyamides

Code	Polymer	T_b(MPa)[b]	E_b(%)[b]	M_i(GPa)[b]
Pm	PMA	64.02	17.0	7.204
B_{M1}[a]	Multiblock 10%	69.06	27.0	5.364
B_{T1}[a]	Triblock 10%	47.23	25.4	3.350
Ny	Nylon-6	45.19	44.0	0.886

[a] B_{T1}, B_{M1}: triblock and multiblock copolyamides (PMA content 10 wt %).

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

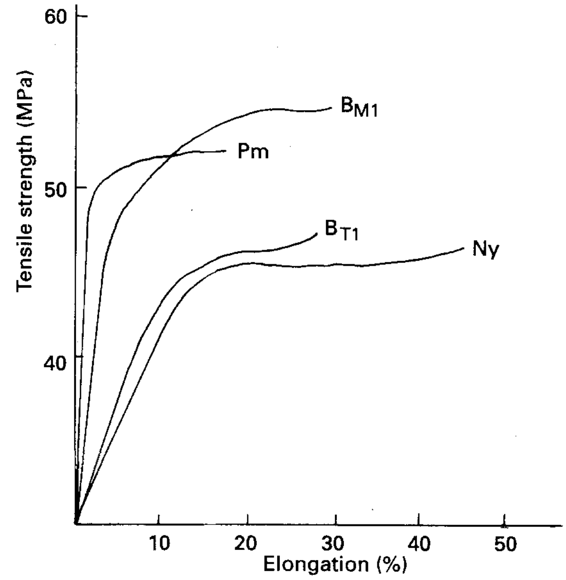


Figure 6 Stress–strain curves for copolyamides: (N_y) nylon-6, (P_m) PMA, (B_{T1}) triblock copolyamide of 10 wt % PMA, (B_{M1}) multiblock copolyamide of 10 wt % PMA.

4. Conclusions

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 semi-rigid PMA proved to be successful. Multiblock copolymers showed, for the same content of PMA, better mechanical properties than those of triblock copolyamides.

From the morphological features, it was demonstrated that a dispersed phase structure was observed in the triblock copolyamides, whereas the multiblock copolyamides exhibited a more homogeneous, compatible structure.

From the DSC analysis it was shown that the semi-rigid PMA-reinforced nylon-6 block copolymer exhibited a higher glass transition temperature (T_g) than that of nylon-6 homopolymer. The T_g and T_m of multiblock copolyamides were even higher than those of triblock copolyamides.

Analysis of X-ray diffraction showed that the triblock copolyamides and nylon-6 homopolymer had two diffraction peaks, i.e. $2\theta = 20$ and 24°. However, the multiblock copolyamides has only one peak at 2θ

= 20°, indicating a different crystal structure of multiblock copolyamides.

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