

Modification of nylon-6 with poly (*m*-phenylene isophthalamide) via MDI as a chain extender

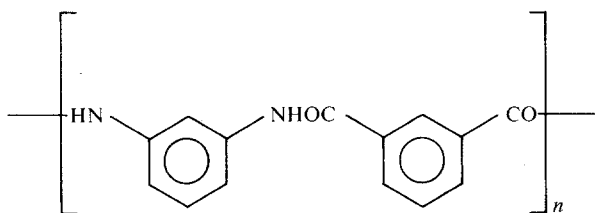
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Reinforcement of flexible nylon-6 by using poly (*m*-phenylene isophthalamide) PmIA (Nomex) using (MDI) 4,4'-diphenylene methane diisocyanate as a chain extender was studied. Observation by scanning electron microscopy showed that the multiblock copolymer had a homogeneous texture. From the differential scanning calorimetry measurements, the multiblock copolymers were shown to have only one melting point, T_m , which is higher than that of nylon-6. The wide-angle X-ray diffraction pattern shows that nylon-6 has two diffraction peaks at $2\theta = 20^\circ$ and 23.8° . However, the multiblock copolymer has only one peak at $2\theta = 20^\circ$, indicating a different crystal structure of multiblock copolymers. The copolymers appear to have a significant reinforcing effect on the mechanical properties.

1. Introduction

Recently, a number of attempts have been made to improve the mechanical properties of the aliphatic nylons by using physical blending and chemical modification with aromatic polyamides such as kevlar, polybenzamide (PBA) [1-4], and poly (4,4'-diphenylsulphone tetraphthalamide) (PSA) [5, 6]. As shown in our previous work [5, 6], the aliphatic nylon-6 was modified by the semi-rigid PSA, exhibiting better thermal and mechanical properties. In our studies, we used wholly rigid polyamide poly (*m*-phenylene isophthalamide) (PmIA) with 4,4'-diphenylene methane diisocyanate (MDI) as a chain extender to reinforce the aliphatic nylon-6. The chemical structure of PmIA (Nomex) is shown below (I).



(I) PmIA (Nomex)

The wholly rigid Nomex has a triclinic crystal structure [7, 8] differing from the monoclinic crystal structure [9-11] of nylon-6. This different crystal structure could affect the crystallization pattern of the copolymers.

2. Experimental procedure

2.1. Materials

Nylon-6 (Formosa Chemical and Fibre Corporation) was first dissolved in formic acid and then poured into an excess amount of water. Samples were refluxed with methanol and hot water for 16 h then dried under vacuum at 100°C for 8 h. The inherent viscosity ($\eta_{inh} = 1.24$) and \bar{M}_n (21 500) of nylon-6 were obtained from the literature [12].

ϵ -Caprolactam, 6-aminohexanoic acid, hexamethylene diamine, 4,4'-diphenylene methane diisocyanate (MDI), *m*-phenylene diamine (MPA), and isophthaloyl dichloride (IPC) (all from Merck Co.) were used as-received.

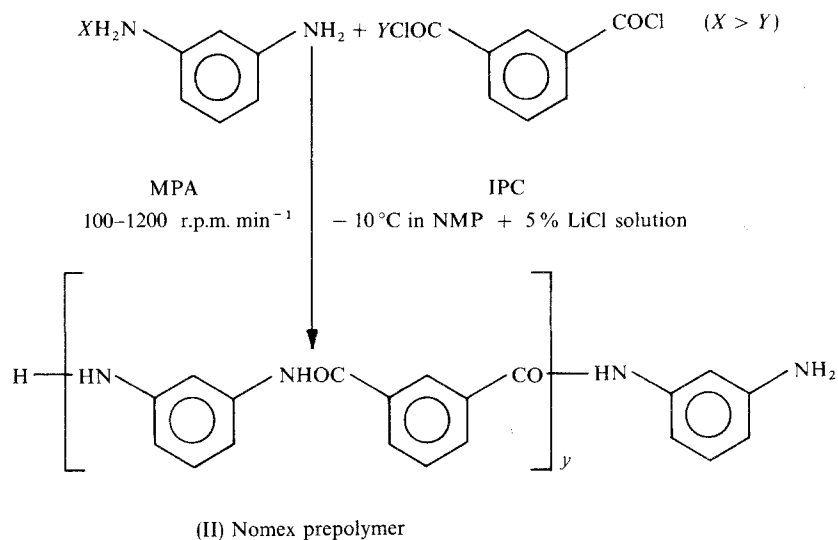
N-methyl-2-pyrrolidone (NMP) was first distilled over CaH_2 at $92-94^\circ\text{C}$ / 14 mm Hg and then stored in the molecular sieves. The moisture content of a 5% LiCl solution in NMP was 0.018 wt %, determined with a Karl-Fischer Moisture Meter, MKA-3, and kyoto Electronic. Lithium chloride (LiCl) was dried under vacuum at 160°C for 5 h.

2.2. Preparation of polyamides and their prepolymers

Low molecular weight diamine-terminated Nomex (PmIA) was polymerized by low-temperature solution polymerization in NMP containing 5% LiCl at -10°C for 30 min. The reaction is shown below (II).

A low molecular weight diamine-terminated nylon-6 prepolymer was prepared by using an excess of hexamethylene diamine (HMDA) as described in the literature [13, 14].

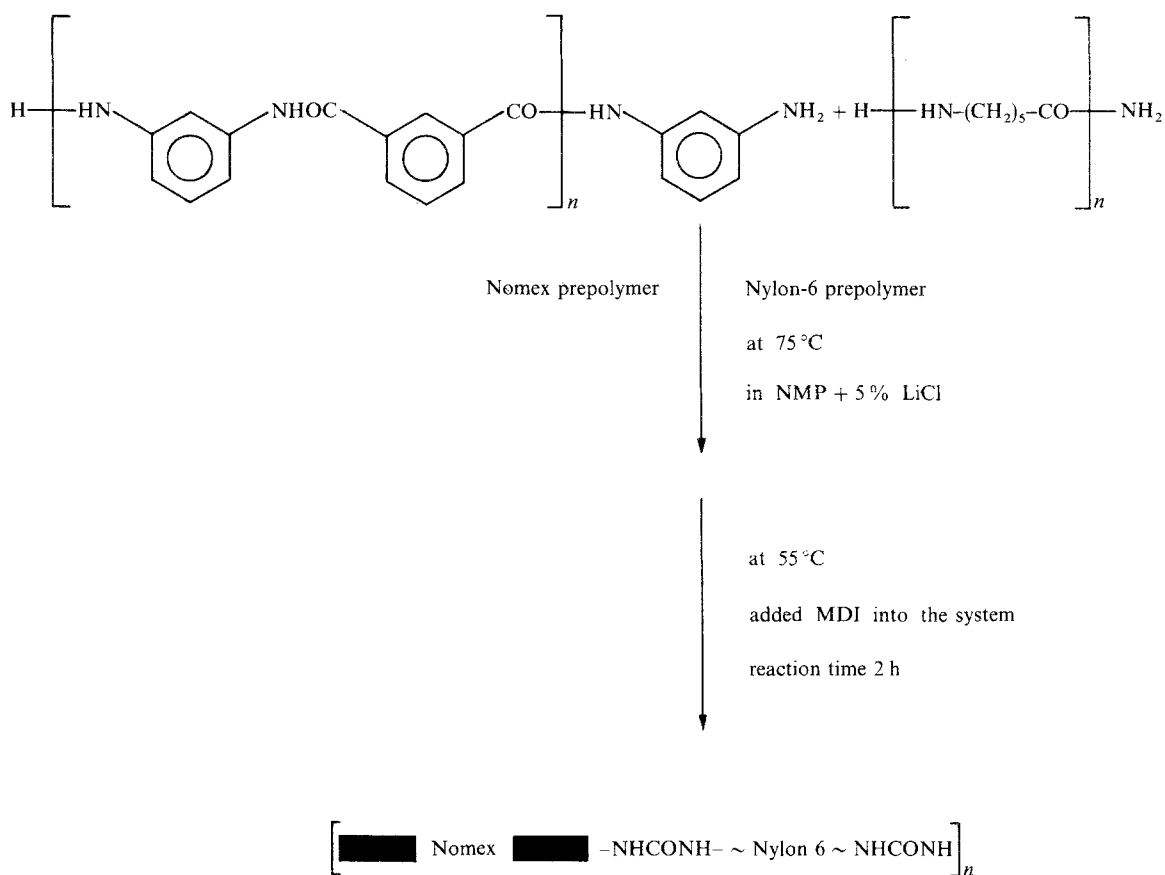
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2.3. Synthesis of nylon-6-MDI-Nomex block copolymers

The copolymers were synthesized by reacting nylon-6 prepolymer and Nomex prepolymer using MDI as a chain extender in the following procedure. The diamine-terminated nylon-6 prepolymer and Nomex prepolymer in NMP + 5% LiCl were mixed and stirred vigorously in a nitrogen atmosphere system at

75-80 °C for 30 min, then allowed to cool down and kept at 50-55 °C. The mixture was then stirred vigorously with MDI for 2 h. Finally, a homogeneous viscous solution was obtained, which was poured into an aqueous solution containing equivalent LiOH. The precipitate was filtered and dried under vacuum at 80 °C for 7 h. The details of the reactions are given below (III).



Multiblock copolyamide of wholly rigid Nomex with nylon-6.

 = Wholly-rigid chain segment of Nomex.

(III)

The various multiblock copolymers were prepared by the solution polymerization of nylon-6 prepolymer with different amounts (wt %) of wholly rigid Nomex prepolymers. The inherent viscosities of the block copolymers were found to be greater than those of the prepolymers; that is, the block copolymers had a higher molecular weight. All nylon-6-MDI-Nomex copolymers are listed in Table I.

2.4. Measurements

Infrared spectra of homopolymers and copolymers were obtained using a Perkin Model 840 Type, over the range 400–4000 cm^{-1} . The samples were films about 10 μm thick. Differential scanning calorimetry (DSC) was used to measure the temperature of crystallization, T_c , in a nitrogen atmosphere using a Du Pont model 9900 DSC, at a heating rate of 20 $^{\circ}\text{C min}^{-1}$, to obtain the glass temperature, T_g , and the melting temperature, T_m . Wide-angle X-ray photographs were taken with nickel-filtered CuK_α radiation using a Rigaku D/max-II Type X-ray diffractometer. A scanning electron microscope, Nanolab 2100, was also used to observe the morphological structures of samples that were sputter-coated with gold to prevent their oxidation. Dynamic viscoelasticity was used to measure the loss tangent, $\tan \delta$, and dynamic modulus E' , with Rheovibron DDV-II-C. All stress-strain data were obtained using the Instron 4201 type testing instrument at an extension rate of 5 mm min^{-1} , and a full load of 50 kg.

3. Results and discussion

3.1. Analysis of infrared spectra

Infrared spectra were obtained by using the thin film technique. The transmission IR spectra of homopolymers and copolymers are shown in Fig. 1. The IR spectra of nylon-6 (curve Ny) are characterized at 3300 cm^{-1} ($=\text{N}-\text{N}$ stretching vibration), 1650 cm^{-1} ($=\text{C}-\text{O}$), 1560 cm^{-1} ($=\text{N}-\text{N}$ deformation), and 2900 and 2770 cm^{-1} ($-\text{CH}_2-$ stretching vibration) absorptions, while the characteristic IR spectra of Nomex (curve Nm) are shown at 3400 cm^{-1} ($=\text{N}-\text{H}$ stretching vibration), 1680 cm^{-1} ($=\text{C}-\text{O}$), 1610 cm^{-1} and 1540 cm^{-1} ($\text{C}-\text{C}$), 1315–1550 cm^{-1} ($=\text{N}-\text{H}$ on metasubstituted) absorptions. The nylon-6-Nomex block copolymers (curves BM_1 – BM_3) show the characteristic absorptions of both nylon-6 and Nomex. Characteristic absorptions of $-\text{CONH}-$ at 1315–1550 cm^{-1} on metasubstituted and 1650 cm^{-1} are noticeable. In addition, nylon-6-Nomex also shows absorptions of $-\text{NHCONH}-$ at 1620–1640 cm^{-1} , emanating from the reaction of the

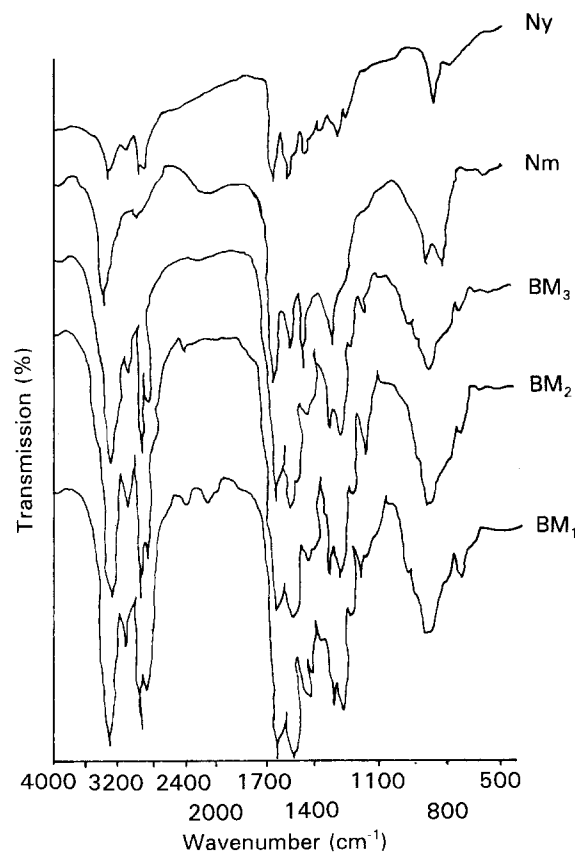


Figure 1 Infrared spectra of homo- and copolyamide films: Ny, nylon-6 homopolymer; Nm, Nomex homopolymer; BM_1 , BM_2 , BM_3 , multiblock copolyamides of 10, 15, and 20 wt % Nomex content.

$-\text{NH}_2-$ on the prepolymer with the $-\text{NCO}$ group of the chain extender.

3.2. Thermal properties of block copolymers

Polymers with aromatic ring structure and cohesive energy 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 behaviour of homopolymers and block copolymers measured by DSC is shown in Fig. 2 and Table II. The results indicate that the glass transition temperature, T_g , and the melting point, T_m , of the block copolymers have increased compared with that of nylon-6. Because the transition temperature could indicate the behaviour of molecular motion within the polymer, it could be used as a clue to identify the phase separation, or the compatibility [12]. The glass transition temperature, T_g , of block copolymers shows only one peak; therefore, a compatible state of wholly rigid Nomex with nylon-6 is possible in the block copolymers. From analysis of the DSC results, the melting temperature of block copolymers is expected to rise with increasing Nomex content. This is the result of the strong hydrogen-bonding connecting the nylon molecule and the nearby urea group, and the immobilization of the immobile structure of MDI. Therefore, the block copolymers exhibit a more regular and wholly crystal structure.

TABLE I Characteristics of block copolyamide

	Nylon-6	10 wt % Nomex	15 wt % Nomex	20 wt % Nomex
$\eta_{\text{inh}}^{(a)}$	0.87	1.07	1.01	0.94

^(a) Measured at a concentration of 0.5 g dl^{-1} in NMP + 5 % LiCl at 30 $^{\circ}\text{C}$.

TABLE II T_g and T_m measured by DSC analysis

	Nylon-6	Nomex	10 wt % Nomex	15 wt % Nomex	20 wt % Nomex
T_g ($^{\circ}\text{C}$)	65	275	84.4	94.7	96.2
T_m ($^{\circ}\text{C}$)	215	> 520	369	374	387

TABLE III d -spacing and crystallite size of nylon-6 and block copolyamide

Code	Polymer form	d (200) (nm)	d (002, 202) (nm)	L (200) (nm)	L (002, 202) (nm)
Ny	Nylon-6	0.440	0.3734	13.2	12.7
BM ₁	Multiblock 10 wt %	0.447	–	10.7	–
BM ₂	Multiblock 15 wt %	0.450	–	11.3	–
BM ₃	Multiblock 20 wt %	0.439	–	11.6	–

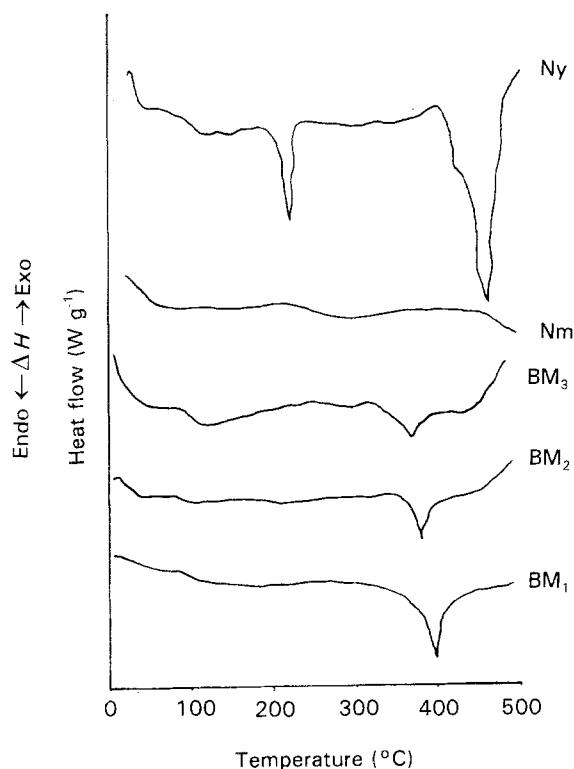


Figure 2 DSC plots of homo- and copolyamide in nitrogen: Ny, nylon-6 homopolymer; Nm, Nomex homopolymer; BM₁, BM₂, BM₃, multiblock copolyamides of 10, 15, and 20 wt % Nomex content.

3.3. Wide-Angle X-ray diffraction

The wide-angle X-ray diffraction patterns of nylon-6 and block copolymers were measured using a Rigaku diffractometer. From the WAXS diffraction patterns in Fig. 3, we know that nylon-6 has two diffraction peaks at $2\theta = 20^{\circ}$ and 23.8° . However, the block copolymer has only one peak at $2\theta = 20^{\circ}$. It is well known that nylon-6 has monoclinic lattices, but Nomex has triclinic lattices [7, 8]. These results evidently indicate a new structure of the block copolymers formed, i.e. the α (200) plane of nylon-6–MDI–Nomex block copolymer in a structure of nylon-6 forms a new crystal structure.

The data in Table III, though, indicate that the d -spacings of nylon-6 and block copolymers are similar, but the crystallite sizes differ from each other. The

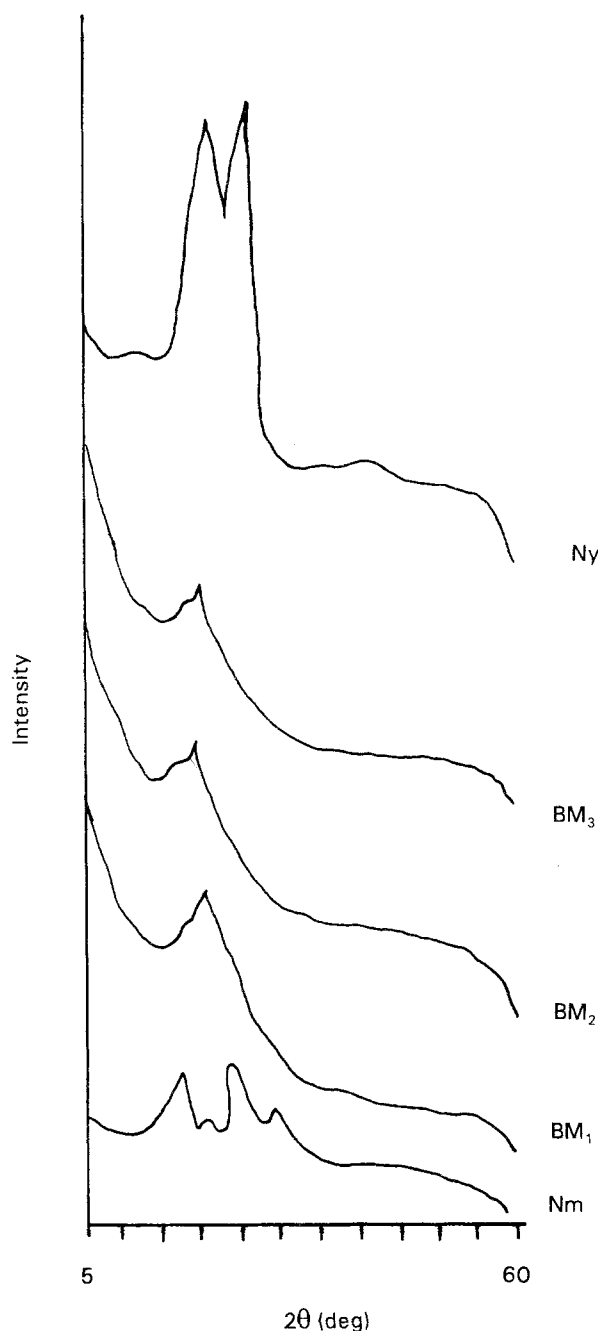


Figure 3 X-ray diagrams of homo- and copolyamide films: Ny, nylon-6 homopolymer; Nm, Nomex homopolymer; BM₁, BM₂, BM₃, multiblock copolyamides of 10, 15, and 20 wt % Nomex content.

crystallite size of the block copolymers is smaller than that of nylon-6.

3.4. Morphological observation

Scanning electron microscopy (SEM) was used to observe the microstructure of the block copolymers. The micrographs in Fig. 4 show the uniform surface structure of the block copolymers, resulting from the covalent molecular chain displaying homogeneous morphology in the block copolymers.

3.5. Mechanical properties of copolymers

The mechanical properties of the block copolymers are shown in Table IV. The tensile strength, T_b , and the initial modulus, M_i , of the block copolymers are

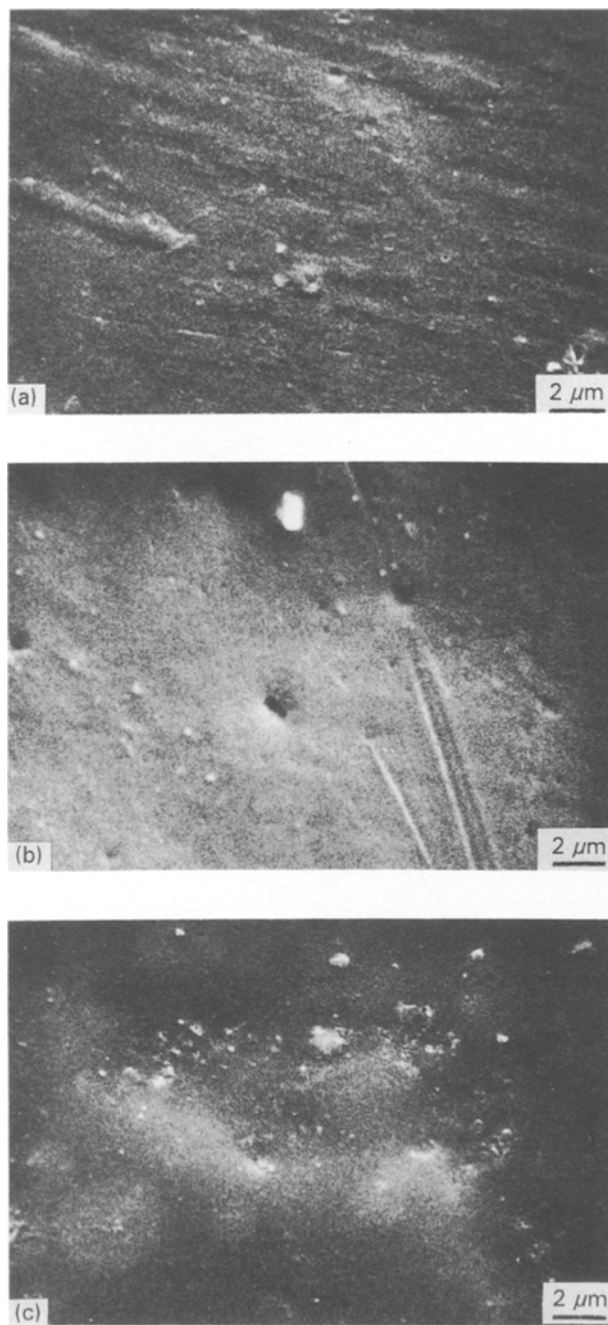


Figure 4 Scanning electron micrographs of multiblock copolyamide of (a) 10 wt % Nomex, (b) 15 wt % Nomex and (c) 20 wt % Nomex contents.

TABLE IV Mechanical properties of nylon-6 and copolyamides

Code	Polymer	T_b (MPa)	E_b (%)	M_i (GPa)
Ny	Nylon-6	45.19	44.0	0.886
BM ₁	Multiblock 10 wt %	60.60	11.6	2.177
BM ₂	Multiblock 15 wt %	55.4	10.8	2.031
BM ₃	Multiblock 20 wt %	54.7	10.4	2.056

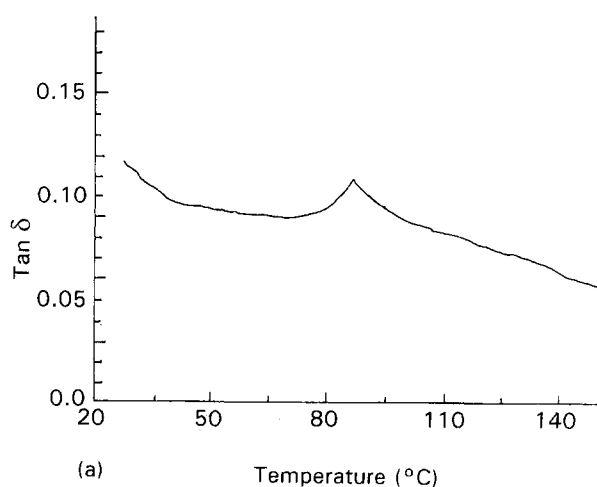
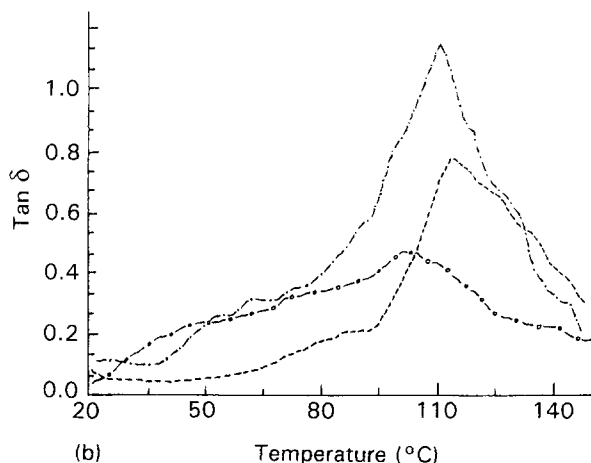


Figure 5 Plots of $\tan \delta$ versus temperature for (a) nylon-6 and its (b) multiblock copolyamides: (—○—) 10 wt %, (—●—) 15 wt %, (···) 20 wt %.

much better than those of nylon-6; and with content of 10 % Nomex in the block copolymers, the best results are obtained. However, the elongation of the block copolymers is reduced. Obviously, nylon-6 is a ductile material originally, but after modification will become a stronger and more brittle material. The ordered block copolymers have better properties not only because of the introduction of wholly rigid units, which caused a higher intramolecular stiffness, but also because of the increase in the intermolecular forces between the polymer chains, thus forming a more uniform and compatible structure.

The loss tangent, $\tan \delta$, and tensile storage modulus, E of nylon-6 and block copolymers are presented in Figs 5 and 6, respectively. Fig. 5 shows that the glass transition temperature, T_g , of block copolymers is higher than that of nylon-6 homopolymer, and rises with increasing Nomex content. This results from the

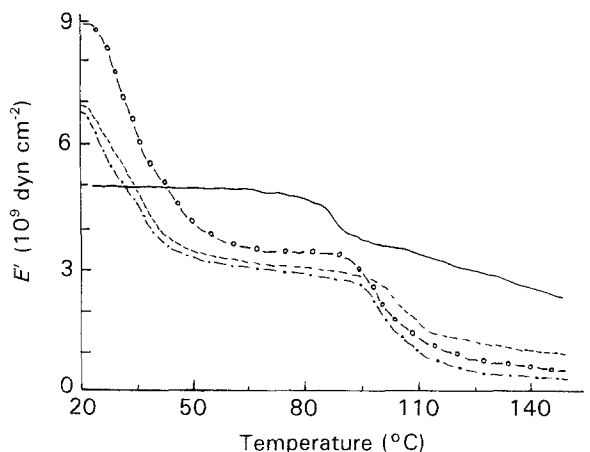


Figure 6 Plots of E' versus temperature for (—) nylon-6 and its multiblock copolyamides: (—○—) 10 wt %, (—●—) 15 wt %, (···) 20 wt %.

resonance-planarity of the aromatic structure which will decrease the free rotation and flexibility of the molecular chain. Although the greater the amount of Nomex the greater will be the aromatic structure of the molecular main chain, Table I shows that the viscosity average molecular weight will decrease with increasing Nomex content. Because of these two factors, the glass temperature, T_g , of 20 wt % Nomex will be slightly higher than that of 15 wt % Nomex.

Fig. 6, shows that mechanical performance is altered in the same way as the tensile test, and will be best when 10 wt % Nomex is added.

4. Conclusions

Three nylon-6–Nomex block copolymers were synthesized by chemical extension using MDI as a chain extender. The reinforcement of nylon-6 with wholly rigid PmIA (Nomex) proved to be successful. Block copolymers could exhibit better thermal and mechanical properties than those nylon-6.

According to the morphological features, the block copolymers exhibit a more homogeneous, compatible structure.

DSC analysis revealed that wholly rigid Nomex-reinforced nylon-6 forming copolymers exhibit both a

higher glass transition temperature and a melting temperature than those of nylon-6 homopolymer; these will increase with addition of Nomex.

Analysis of wide-angle X-ray diffraction patterns shows that nylon-6 homopolymer has two diffraction peaks at $2\theta = 20^\circ$ and 23.8° . However, the block copolymers have only one peak at $2\theta = 20^\circ$, indicating a different crystal structure of the block copolymers.

From measurement of the mechanical properties, the mechanical properties of block copolymer were found to be excellent compared with those of nylon-6 homopolymer, but 10 wt % Nomex was the best. Therefore, the optimum Nomex content in nylon-6 is suggested to be 10 wt %.

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