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Modification of polyurethane with wholly-rigid poly (*m*-phenylene isophthalamide)

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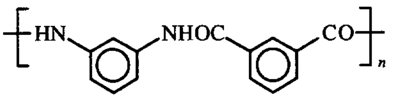
Flexible polyurethane (PU) was reinforced by wholly-rigid aromatic polyamide poly (*m*-phenylene isophthalamide) (PmIA) (Nomex) by physical polyblending and chemical copolymerization. Three polyurethane elastomers were blended physically with various amounts of high molecular weight Nomex to form twelve PU/Nomex polyblends in order to modify their physical properties. Also three multiblock copolyamides (PU–Nomex)were synthesised with a low molecular weight diamine-terminated Nomex prepolymer as a hydrogen donor for chain extending. From differential scanning calorimetry and Rheovibron measurements it was shown that both the polyblends and multiblock copolyamides exhibited a glass transition temperature under 0 °C and had a higher storage modulus, *E′*, than those of the polyurethane. Scanning electron microscopy revealed that the polyblends and multiblock copolyamides had a dispersed phase structure. From the wide-angle X-ray diffraction pattern of the polyurethane and multiblock copolyamides it was found that the degree of stress-induced crystallization was dependent on the composition of the soft and hard segments and also the degree of its stretching. With regard to mechanical properties, it was found that both the tensile strength and elongation of the multiblock copolyamides had a more significant reinforcing effect than those of the polyblends and polyurethanes.

1. Introduction

Recently, a number of attempts were made to improve the mechanical properties of polyurethane (PU) by using physical blending and chemical modification with aromatic polyamides such as poly(4,4′-diphenylsulphone terephthalamide) (PSA). As shown previously [1–3], PU when modified by semi-rigid PSA, exhibits better thermal and mechanical properties. In this study the chemical incorporation of wholly-rigid polyamide poly(*m*-phenylene isophthalamide) (PmIA) (Nomex) blocks into polyurethane segments also resulted in improvement. Because of its excellent solubility [4] and thermal stability [5, 6], wholly-rigid Nomex was selected to strengthen the mechanical and thermal properties of polyurethane. The chemical structure of Nomex is [7, 8]:



Another reason for selecting Nomex for reinforcement was that it can easily form strong intermolecular hydrogen bonding with PU, and therefore good molecular compatibility was expected.

2. Experimental procedure

2.1. Materials

4,4′-Diphenylmethane diisocyanate (MDI) was obtained from the Dynasty Chemical Corporation, polytetramethylene glycols (PTMG 1000, 2000, 2900) from the Evermove Chemical Co., and 1,4-butane diol (BD) from the Ferak Berlin Chemical Co. Isophthaloyl dichloride (IPC), *m*-phenylene diamine (MPA) and dimethyl acetamide (DMAc) were purchased from the Merck Co., and used as-received.

N-methyl-2-pyrrolidone (NMP) was first distilled over CaH_2 at 92–94 °C/14 mm Hg and stored in molecular sieves. The moisture content of 5% LiCl solution in NMP was 0.018 wt % as measured 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

High molecular weight wholly-rigid Nomex (PmIA) was polymerized by low-temperature solution polymerization in *N*-methyl-2-pyrrolidone (NMP) containing 5% LiCl at − 15 °C for 30 min [5, 9, 10] (Reaction 1)

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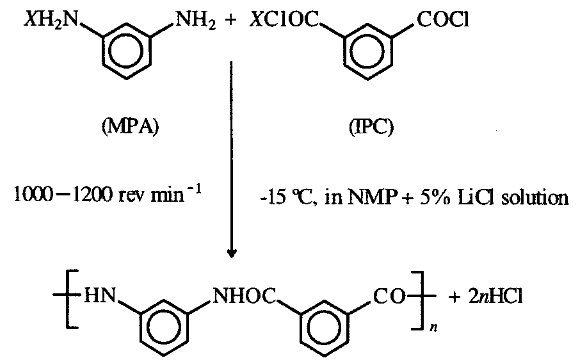
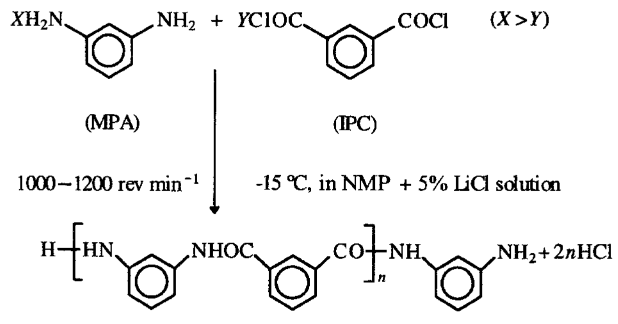


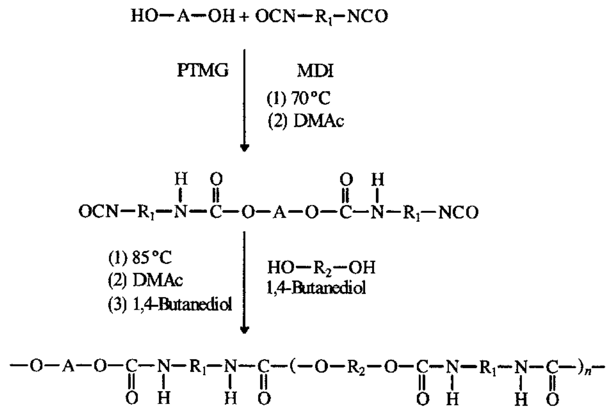
Nomex (PmIA) (1)

Similarly, the low molecular weight Nomex was also prepared by excess *m*-phenylene diamine (MPA) with isophthaloyl dichloride (IPC) in *N*-methyl-2-pyrrolidone (NMP) + 5%LiCl solution at $-15\,^{\circ}C$ for 30 min, i.e.



Aromatic diamine-terminated Nomex (2)

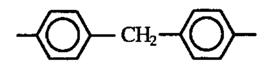
The polyurethanes were prepared as follows. A 250 ml five-necked flask was equipped with a dropping funnel, nitrogen gas inlet, mechanical stirrer and thermometer. MDI was dissolved in 30 ml dimethyl acetamide (DMAc) and heated to 65 °C. Then PTMG in 15 ml DMAc was slowly added to the previous solution with vigorous stirring over 30 min, and the temperature was further increased to 70 °C. The reaction time varied according to the different molecular weights of PTMG. For weights of 1000, 2000, and 2900, reaction times were 40, 70, and 80 min, respectively. Finally, 1,4-butanediol (BD) in 15 ml DMAc was added slowly and heated to 85 °C. After reaction for 50 min the solution was cooled slightly and continuously stirred for 90 min. When the reaction stopped a viscous solution was obtained, and the polymers were cast into films from the solution. The properties of the polymers listed in Table I. The reaction scheme is as follows [11]



Polyurethane elastomer (3)

where A is $-[(CH_2)_4-O]_n-$

R_1 is



and R_2 is $-(CH_2)_4-$

2.3. Blends of aramid Nomex and conventional PU

Three polyurethanes (PU–1000–BD, PU–2000–BD and PU–2900–BD) were blended physically with high molecular weight Nomex in different ratios (5, 10, 15 and 20 wt %) to form twelve PU/Nomex polyblends (Table II). The mixture was dissolved in NMP and

TABLE I Element analysis and inherent viscosity of polyblends and block copolyamides

Code	Polymer	Molar ratio	Element analysis (%) C	H	N	η^{d}_{inh}
M_1	PU–1000–BD[a]	12:1	65.19	9.14	3.85	0.34
M_6	PU–2000–BD	1:2:1	64.76	9.29	3.29	0.32
M_{11}	PU–2900–BD	1:2:1	63.74	9.36	2.72	0.31
B_1	PU–1000–Nomex	1:2:1	66.21	9.69	3.98	0.43
B_2	PU–2000–Nomex	1:2:1	65.78	9.82	3.76	0.42
B_3	PU–2900–Nomex	1:2:1	65.26	9.68	3.68	0.40
N_m	Nomex[c]	—	68.32	8.45	4.26	1.06

[a] Polyurethane molar ratio, PTMG (1000):MDI:1,4-BD = 1:2:1.
[b] Multiblock copolyamides molar ratio, PTMG (1000):MDI: Nomex prepolymer = 1:2:1.
[c] High-molecular weight Nomex polymer.
[d] Determined in conc. H_2SO_4 (98%) at 30 °C.

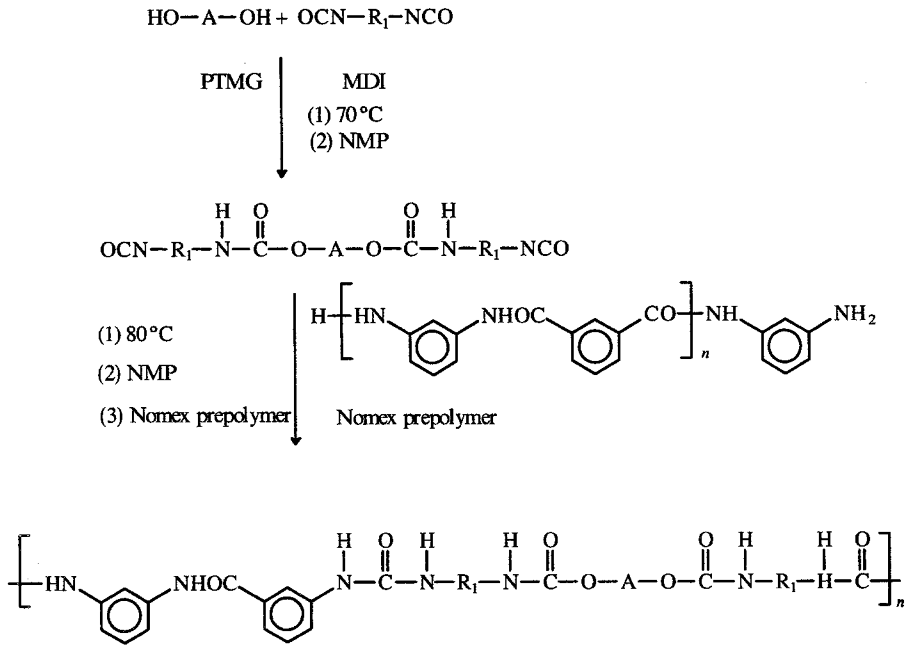
TABLE II Compositions of PU/Nomex polyblends

Code	Polyblend	Nomex (wt %)
M_1	PU–1000–BD/Nomex	0
M_2	PU–1000–BD/Nomex	5
M_3	PU–1000–BD/Nomex	10
M_4	PU–1000–BD/Nomex	15
M_5	PU–1000–BD/Nomex	20
M_6	PU–2000–BD/Nomex	0
M_7	PU–2000–BD/Nomex	5
M_8	PU–2000–BD/Nomex	10
M_9	PU–2000–BD/Nomex	15
M_{10}	PU–2000–BD/Nomex	20
M_{11}	PU–2900–BD/Nomex	0
M_{12}	PU–2900–BD/Nomex	5
M_{13}	PU–2900–BD/Nomex	10
M_{14}	PU–2900–BD/Nomex	15
M_{15}	PU–2900–BD/Nomex	20

stirred vigorously. Then the solutions were cast on a glass plate and dried under vacuum at 80 °C for 16 h to prepare the films.

2.4. Synthesis of PU–Nomex block copolymers

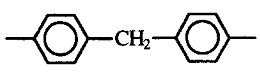
Three multiblock copolyamides (PU–1000–Nomex, PU–2000–Nomex, PU–2900–Nomex) were synthesised by using Nomex prepolymer as a hydrogen donor for chemical extension. The reaction scheme is as follows [11]



Multiblock copolyamides of wholly-rigid Nomex with polyurethane.

where A is $\left[(CH_2)_4-O\right]_m$

and R_1 is



MDI was dissolved in 30 ml NMP and heated to 65 °C. Then PTMG in 15 ml NMP was slowly added to the previous solution with vigorous stirring over 30 min. The temperature varied according to the molecular weight of PTMG. For molecular weights of 1000, 2000, and 2900, reaction times were 40, 70, and 80 min, respectively. Then Nomex prepolymer in 30 ml NMP was added slowly and heated to 80 °C. After 2 h the solution was cooled slightly and continuously stirred for 90 min. When the reaction stopped multiblock copolyamides were obtained. The inherent viscosity and element analysis of the synthesis are given in Table I. The inherent viscosity of polymer in 98% sulphuric acid was 0.04 d g^{-1} at 30 °C. Elemental analysis was performed using a Perkin–Elmer 240C EA. The number average molecular weight, $\bar{M}_n$, of Nomex prepolymer was about 800, as measured by gel-permeation chromatography (GPC).

2.5. Measurements

Infrared (IR) spectra of homopolymers and copolymers were obtained with a Hitachi Model 260-50, over the range 250–4000 m^{-1}. The samples were in the form of film of about 10 μm thickness. Elemental analysis (C,H,N) was performed using a Perkin–Elmer 240C EA.

Dynamic mechanical measurements were performed at −100 °C to room temperature and from room temperature to 250 °C with a DDV II-C-type Rheovibron. Some samples purged with dry air were cooled by liquid nitrogen in the first range, and others purged with dry nitrogen gas in the second range. Measurements were made at 2 °C min^{-1} with 20 mm length, 4 mm width and 0.4 mm thickness specimens.

Differential scanning calorimetry (DSC) was performed with a Seiko SSC 5000 at 20 °C min^{-1} in a nitrogen atmosphere to obtain the glass transition temperature, T_g, and melting temperature, T_m.

Wide-angle X-ray photographs were taken by nickel-filtered CuKα 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 gold to prevent their oxidation.

All stress–strain data were obtained with an Instron 1122 at an extension rate of 10 mm min^{-1} and full load of 10 kg, and specimen dimensions of 50 mm length, 10 mm width and 0.5 mm thickness.

3. Results and discussion

3.1. Analysis of IR spectra

IR spectra were obtained using the thin-film technique. The transmission IR spectra of homopolymers and multiblock copolyamides are shown in Fig. 1. The IR spectrum of polyurethane (curve M_1) was characterized at 3400 cm^{-1} (N–H stretch vibration), 1700 cm^{-1} (C=O), 2940 cm^{-1} (-CH stretch

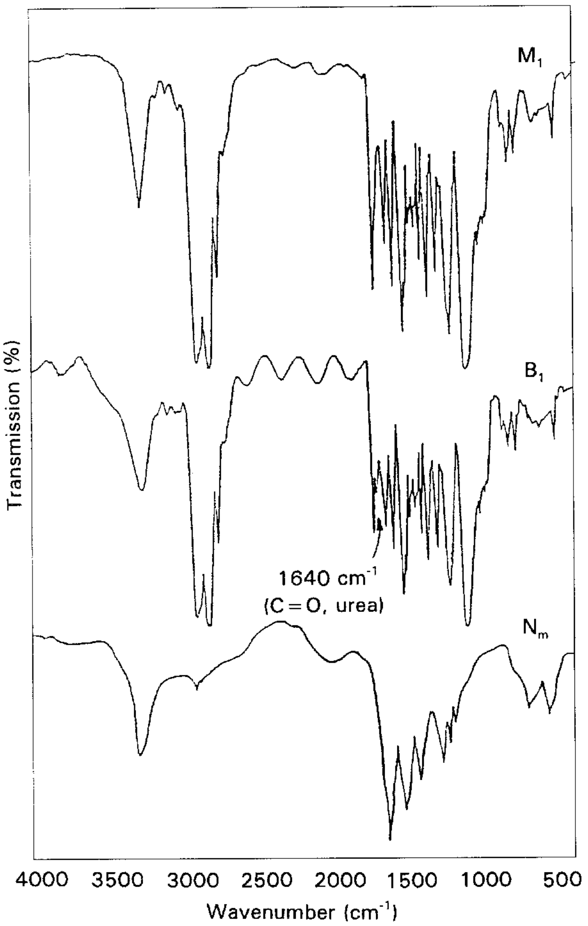


Figure 1 Infrared spectra of polyurethane and multiblock copolyamide films: N_m, Nomex 100 wt %; M_1, Nomex 0 wt %; B_1, Nomex 36 wt %.

vibration), and 1560 cm^{-1} (N–H deformation) absorptions. The characteristic IR spectra of Nomex (curve N_m) were shown at 3400 cm^{-1} (N–H stretch vibration), 1680 cm^{-1} (C=O), 1610 cm^{-1} and 1540 cm^{-1} (C$\overline{\cdots}$C), 1315–1550 cm^{-1} (N–H on metasubstituted), and 3000–3150 cm^{-1} (N–H on parasubstituted) absorptions. The multiblock copolyamide (curve B_1) showed both the characteristic absorption of polyurethane and Nomex.

The characteristic absorption of the C=O of urea group (–NHCONH–) found at about 1640 cm^{-1} for the multiblock copolyamide (curve B_1). This came from the reaction of the –NCO– on paraposition of benzene with the metaposition –NH_2 group of the Nomex prepolymer.

3.2. Dynamic mechanical properties of block copolymers and polymer blends

The temperature-dependence of loss tangent, tan δ, and storage modulus, E', for the PU–1000–BD/Nomex polyblend in the higher temperature range are shown in Table III and Fig. 2. It was found that the primary dispersion temperature, T_α, of PU–1000–BD (M_1), which corresponds to the glass temperature of the hard butyl segment (the short $\left(\text{MDI-BD}\right)_n$ segment), T_{gh}, was about 63 °C and would shift to a higher temperature region with an increase in wholly-rigid Nomex. In addition, the storage modulus, E', of the polyblends was also found to increase with increased Nomex. These facts demonstrated that the micro-Brownian motion of the hard butyl segment in PU was restrained by the presence of wholly-rigid Nomex molecules; and then a higher T_{gh} and modulus, E', would occur. Similarly, the damping properties of other polyblends (M_6–M_{15}) were also found to have the same tendency in the high temperature range.

With regard to the second dispersion temperature, T_β, of polyblends in the lower temperature range, corresponding to the glass transition temperature of the soft PTMG segment, T_{gs} which is shown in Table III and Fig. 3, T_{gs} also increased in the presence of Nomex. The temperature shift was appreciable due to the soft PTMG segment being immobilized by both the hard butyl and the wholly-rigid Nomex segment. Other dynamic mechanical characteristics of other polyblends (M_6–M_{15}) were similar to those of the PU–1000–BD/Nomex polyblend series.

As seen in Table III and Fig. 4, multiblock copolyamides had a lower T_{gs}, which was close to that of the pure soft PTMG segment, and indicates that the soft matrix of the multiblock copolyamides was much self-aggregated. This characteristic could be verified by the effect of the molecular weight of the soft segment on the degree of phase separation, which was found that the higher molecular weight could cause better self-phase aggregation and then a lower T_{gs}, and storage modulus, E'.

3.3. Thermal properties of block copolymers and polymer blends

The thermal properties of polyblends and multiblock copolyamides which were measured by DSC are shown in Table III. Comparing the T_{gs} for DSC with that for Rheovibron, it was found that the T_g for the former was higher than for the latter. The heating rate was considered to be a contributing factor. The DSC rate was 20 °C min^{-1}, and the Rheovibron rate was 2 °C min^{-1}. It can be seen from Fig. 5 that the PU–2000–BD/Nomex polyblend series showed an increase in T_g with increased Nomex. This indicated that the micro-Brownian motion of the hard butyl segment in PU–2000–BD did suffer from the restraint of the wholly-rigid Nomex molecules, especially when the amount of Nomex was increased. Surprisingly, it was found that the T_m of the polyblends did not change much, remaining at about 185 °C for the PU–2000–BD/Nomex polyblend series (M_6–M_{10}) [12].

The DSC analysis for multiblock copolyamides is shown in Fig. 6 with various molecular weights of soft segment; due to the lower T_{gs} it was evident that the degree of phase separation of B_2 and B_3 was greater than that of B_1. The melting endotherm peak, T_{ms}, of the soft segment appeared at 9 and 12° C in B_2 and B_3, indicating long-chain crystallization of the soft segment, which was not seen in B_1. The T_{ms} of other

TABLE III Thermal properties of polyblends and block copolyamides

Code	Polymer	Nomex (wt %)	$T_{gs}^{(a)}$		$T_{ms}^{(c)}$	$T_{gh}^{(d)}$		T_m	$T_d^{(e)}$
			R[b]	DSC		R	DSC		
M_1	PU-1000-BD/Nomex	0	− 36	− 32	—	63	76	164	272
M_2	PU-1000-BD/Nomex	5	− 30	− 26	—	70	80	165	272
M_3	PU-1000-BD/Nomex	10	− 25	− 21	—	78	87	166	273
M_4	PU-1000-BD/Nomex	15	− 19	− 14	—	86	95	166	274
M_5	PU-1000-BD/Nomex	20	− 13	− 11	—	95	102	166	274
M_6	PU-2000-BD/Nomex	0	− 46	− 43	10	60	72	183	261
M_7	PU-2000-BD/Nomex	5	− 43	− 40	11	60	76	184	261
M_8	PU-2000-BD/Nomex	10	− 37	− 38	11	73	80	185	262
M_9	PU-2000-BD/Nomex	15	− 31	− 33	11	81	86	185	263
M_{10}	PU-2000-BD/Nomex	20	− 25	− 26	13	88	94	186	264
M_{11}	PU-2900-BD/Nomex	0	− 58	− 52	20	58	65	194	250
M_{12}	PU-2900-BD/Nomex	5	− 55	− 49	22	62	69	194	251
M_{13}	PU-2900-BD/Nomex	10	− 51	− 45	22	68	75	196	252
M_{14}	PU-2900-BD/Nomex	15	− 46	− 40	23	77	81	196	252
M_{15}	PU-2900-BD/Nomex	20	− 42	− 36	24	82	86	196	253
B_1	PU-1000-BD/Nomex	36	− 44	− 35	—	—	263	350	343
B_2	PU-2000-Nomex	25	− 47	− 40	9	—	276	352	345
B_3	PU-2900-Nomex	20	− 51	− 45	12	—	292	356	356
N_m	Nomex	100	—	—	—	—	285	> 520	—

[a] T_g of soft segment.
[b] Rheovibron.
[c] T_m of soft segment phase.
[d] T_g of hard segment (butyl or Nomex segment).
[e] Decomposition temperature, measured by TGA.

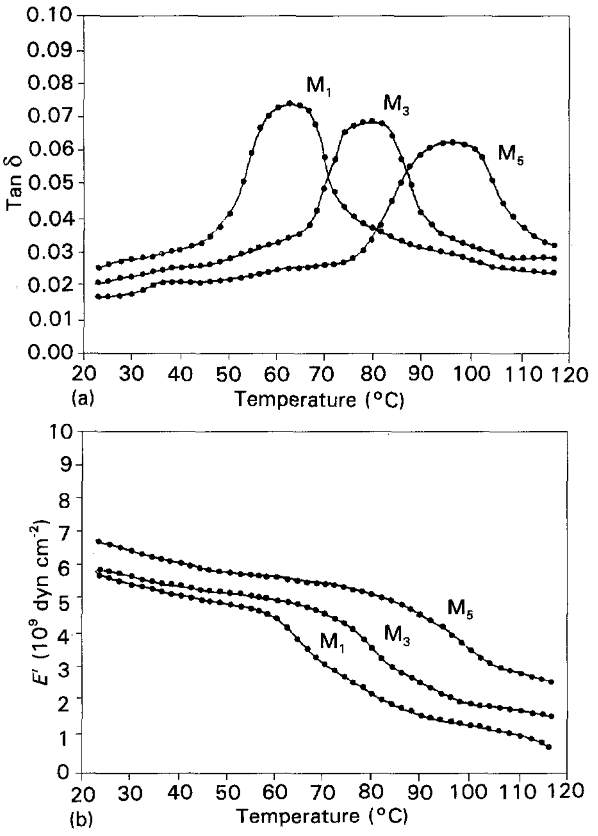


Figure 2 Temperature-dependence of tan δ and storage modulus, *E*, in higher temperature range for PU-1000-BD/Nomex polyblend series at 110 Hz: M_1, 0 wt % Nomex; M_3, 10 wt % Nomex; M_5, 20 wt % Nomex.

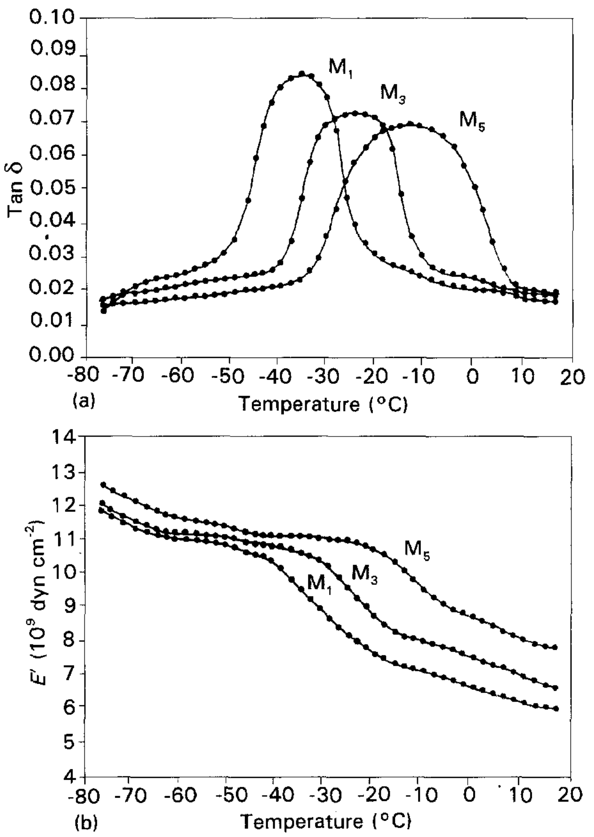


Figure 3 Temperature-dependence of tan δ and storage modulus, *E*, in lower temperature range for PU-1000-BD/Nomex polyblend series at 110 Hz: M_1, 0 wt % Nomex; M_3, 10 wt % Nomex; M_5, 20 wt % Nomex.

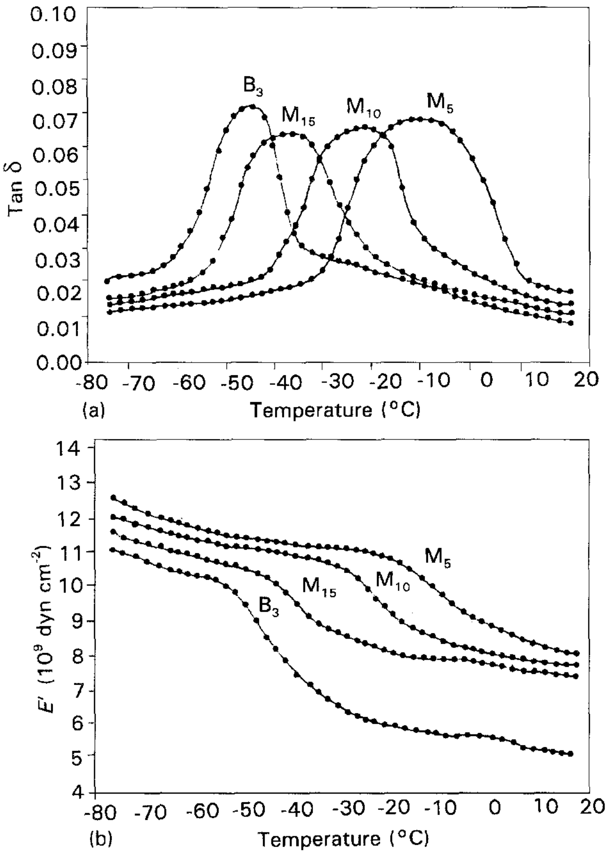


Figure 4 Temperature-dependence of tan δ and storage modulus, *E*, in lower temperature range for polyblends (M_5, M_{10}, M_{15}) and multiblock copolyamide (B_3) at 110 Hz: M_5, 20 wt % Nomex; M_{10}, 20 wt % Nomex; M_{15}, 20 wt % Nomex; B_3, 20 wt % Nomex.

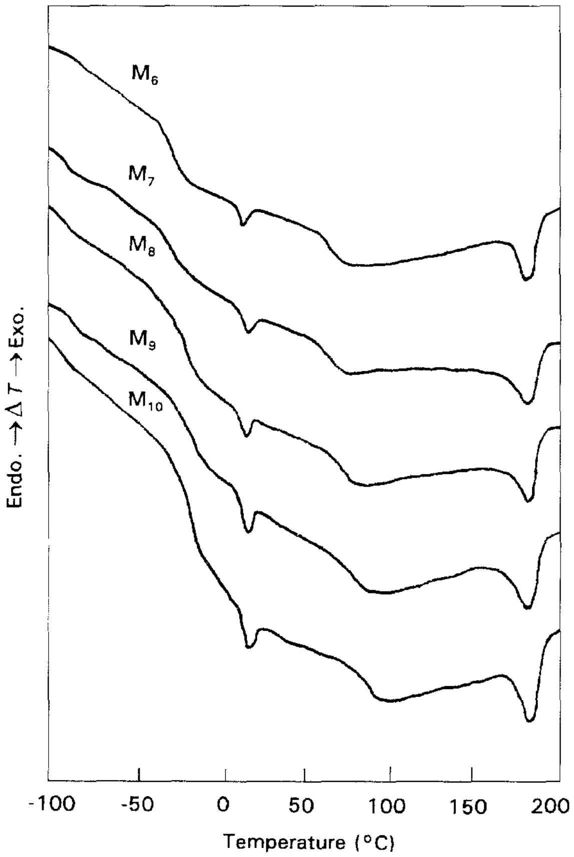


Figure 5 DSC plots of polyblends of PU-2000-BD with Nomex in nitrogen: M_6, 0 wt % Nomex; M_7, 5 wt % Nomex; M_8, 10 wt % Nomex; M_9, 15 wt % Nomex; M_{10}, 20 wt % Nomex.

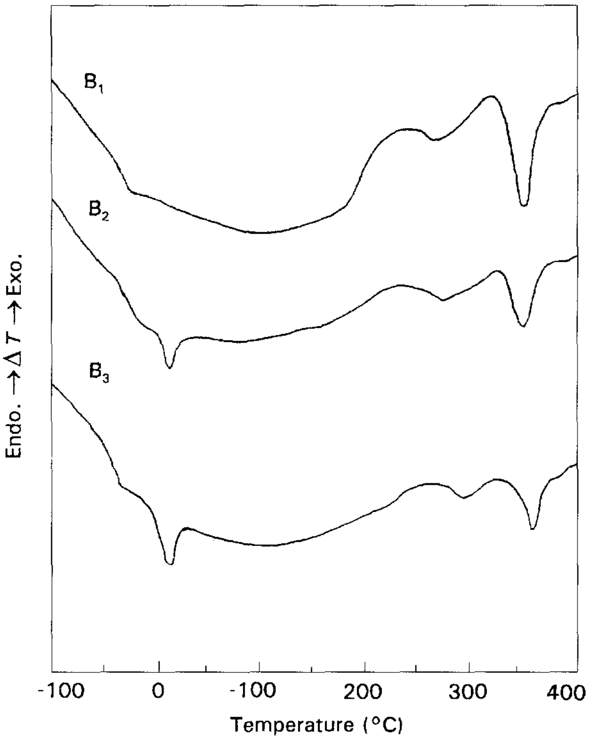


Figure 6 DSC plots of multiblock copolyamides B_1(PU-1000/Nomex), B_2(PU-2000/Nomex), B_3(PU-2900/Nomex).

polyblends (M_6–M_{15}) was also found to have the same tendency in the thermal properties. In general, the thermal properties of multiblock copolyamides were superior to those of polyblends and polyurethane.

3.4. Wide-angle X-ray diffraction

From the WAXS diffraction patterns in Figs 7–9 it was found that the unstretched PU-2000–BD (M_6) had only one diffraction peak, i.e. $2\theta = 20°$, as also did unstretched PU-2000–Nomex (B_2), which was consistent with the results of others [13–16]. Thus, it was concluded that the diffraction peak at $2\theta = 20°$ could come from the diffraction of soft PTMG segment in the (1 0 0) plane [13]. In addition, a clear shoulder at about $2\theta = 24°$ was found for the multiblock copolyamides under 600% stretching, but no shoulder was found for the PU–1000–Nomex (B_1). This shoulder was pertained to be the diffraction peak in the (0 1 0) plane of soft PTMG segment [13]. The degree of stress-induced crystallization was known to be dependent on both the segmental composition of the soft and hard segments and also its degree of stretching [14]. In addition, because the half-width of the diffraction peak was narrowed by stretching, it was evident that the crystallization of the multiblock copolyamides became more perfect after stretching.

3.5. Morphological observation

Scanning electron microscopy (SEM) was used to examine the microstructure of the polyblends and multiblock copolyamides. Fig. 10a shows a uniform surface structure for PU (PU–1000–BD, i.e. M_1), but

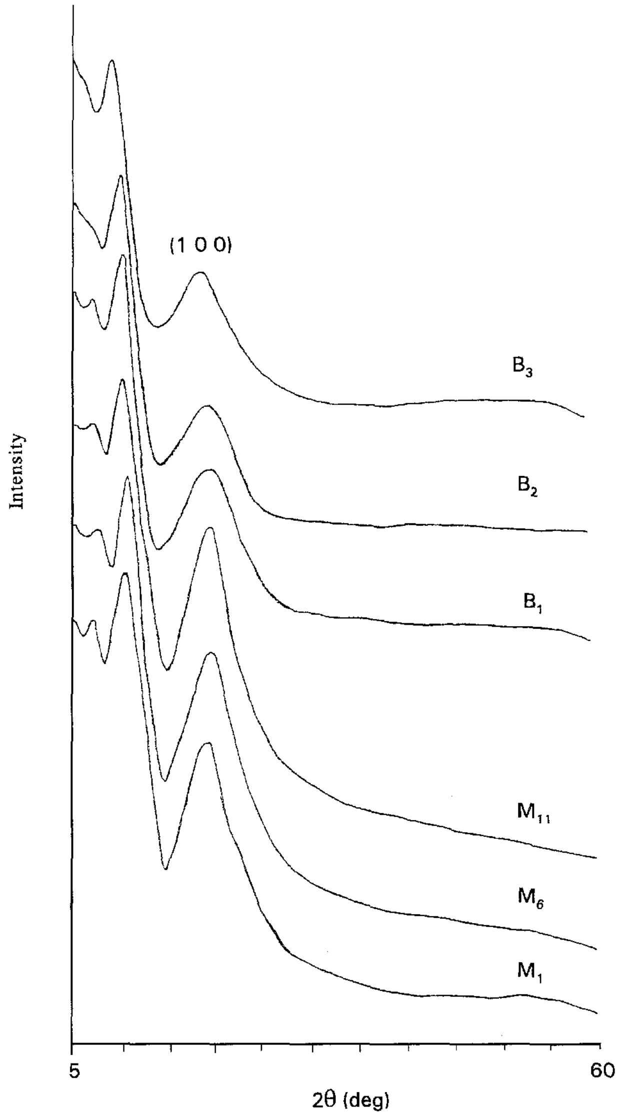


Figure 7 X-ray diagrams of unstretched PU and multiblock copolyamide films: M_1(Nomex 0 wt %); M_6(Nomex 0 wt %); M_{11}(Nomex 0 wt %); B_1(Nomex 36 wt %); B_2(Nomex 25 wt %); B_3(Nomex 20 wt %).

the polyblends showed dispersed grain size as the amount of Nomex was increased (Fig. 10b and c). The grain particles were considered to be aggregates of Nomex. When the Nomex content was 20 wt % the polyblends (M_5) showed large grain size (2–4 μm diameter). Similarly, other polyblends also exhibited morphology of the same aggregation. This indicates that the dispersed phase of Nomex in the polyblend is incompatible with PU and has a tendency to decrease its interfacial area [17–19].

From SEM it is shown in Fig. 11a and b that the morphology of the multiblock copolyamides also exhibited a dispersed phase structure as in the polyblends. The dispersed phase texture of the multiblock copolyamides could not be broken by any solvent, indicating that polyurethane and Nomex were combined by the covalent bonds in the multiblock copolyamides.

3.6. Mechanical properties of polyblends and block copolymers

Mechanical properties of the polyblends and multiblock copolyamides are presented in Table IV, and Fig. 12. With regard to the PU–1000–BD/Nomex (M_1) polyblend series, it was found that the tensile strength increased initially and then decreased. This is consistent with aforementioned results of morphological observation. With lower Nomex content the polyblends exhibit a dispersed small grain particle structure. The tensile strength of various polyblends of polyurethane (M_1–M_5) was found to increase gradually as Nomex was increased. This trend may result from the immobility and rigidity of the aggregated Nomex domain, and also the increase of the intermolecular hydrogen bonding between the wholly-rigid Nomex and hard butyl segment. Moreover, it was observed that the blends containing more than 10 wt % Nomex exhibited a continuous reduction of

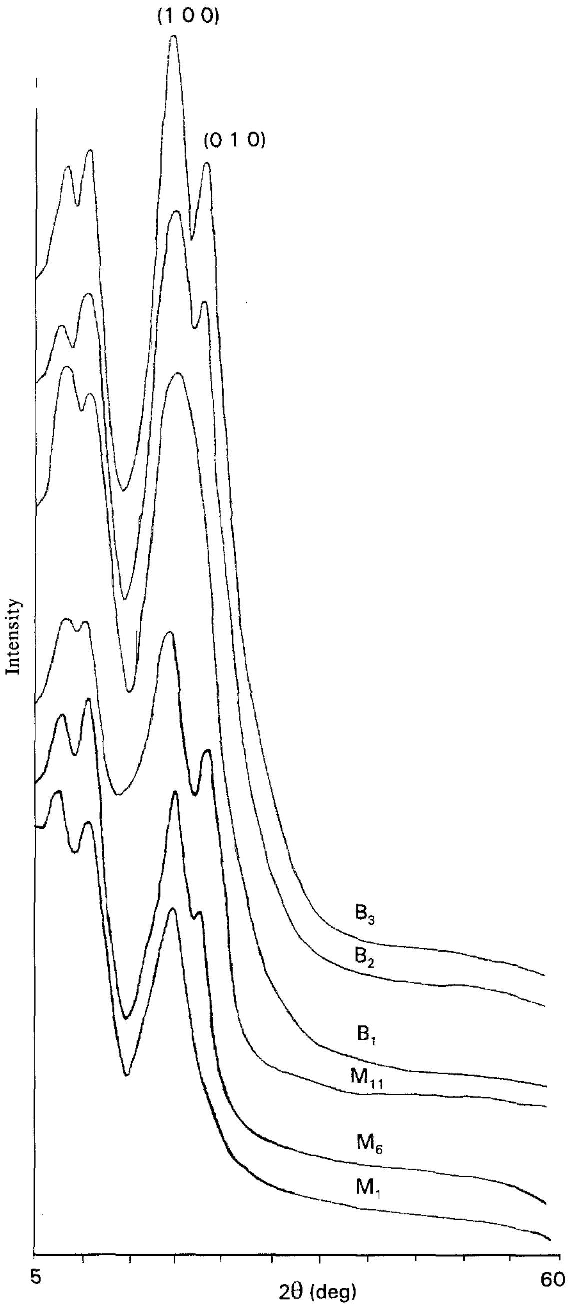


Figure 8 X-ray diagrams of stretched PU and multiblock copolyamide films: M_1(Nomex 0 wt %); M_6(Nomex 0 wt %); M_{11}(Nomex 0 wt %); B_1(Nomex 36 wt %); B_2(Nomex 25 wt %); B_3(Nomex 20 wt %).

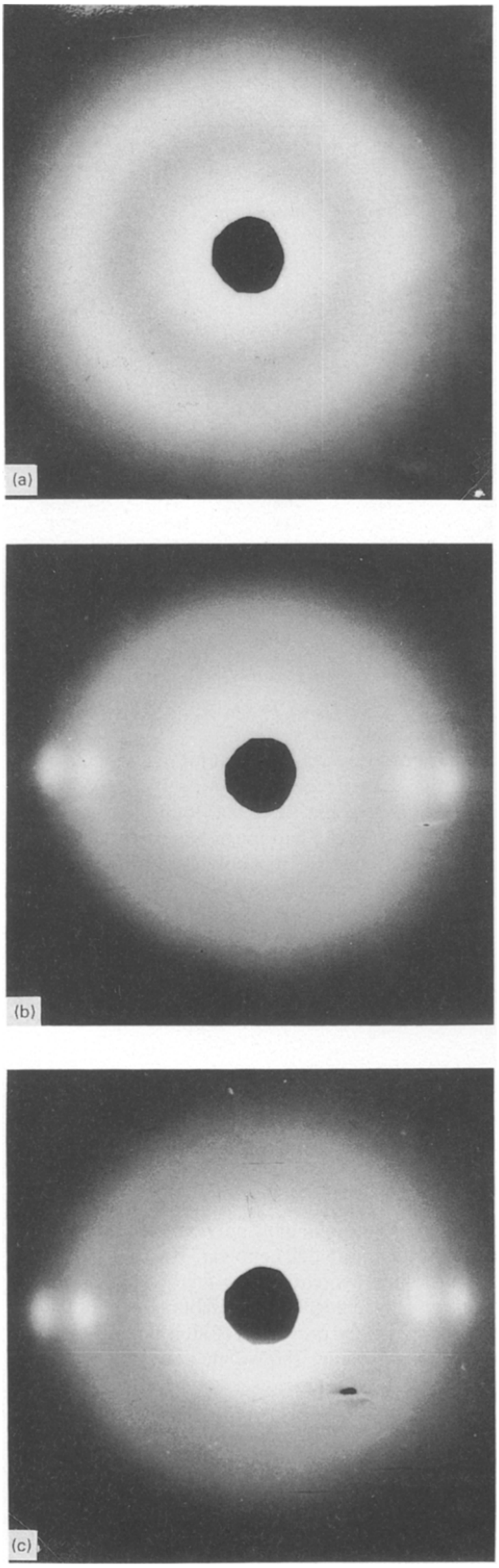


Figure 9 WAXS patterns of multiblock copolyamides: (a) B_2(drawn 0%); (b) B_2(drawn 300%); (c) B_2(drawn 600%).

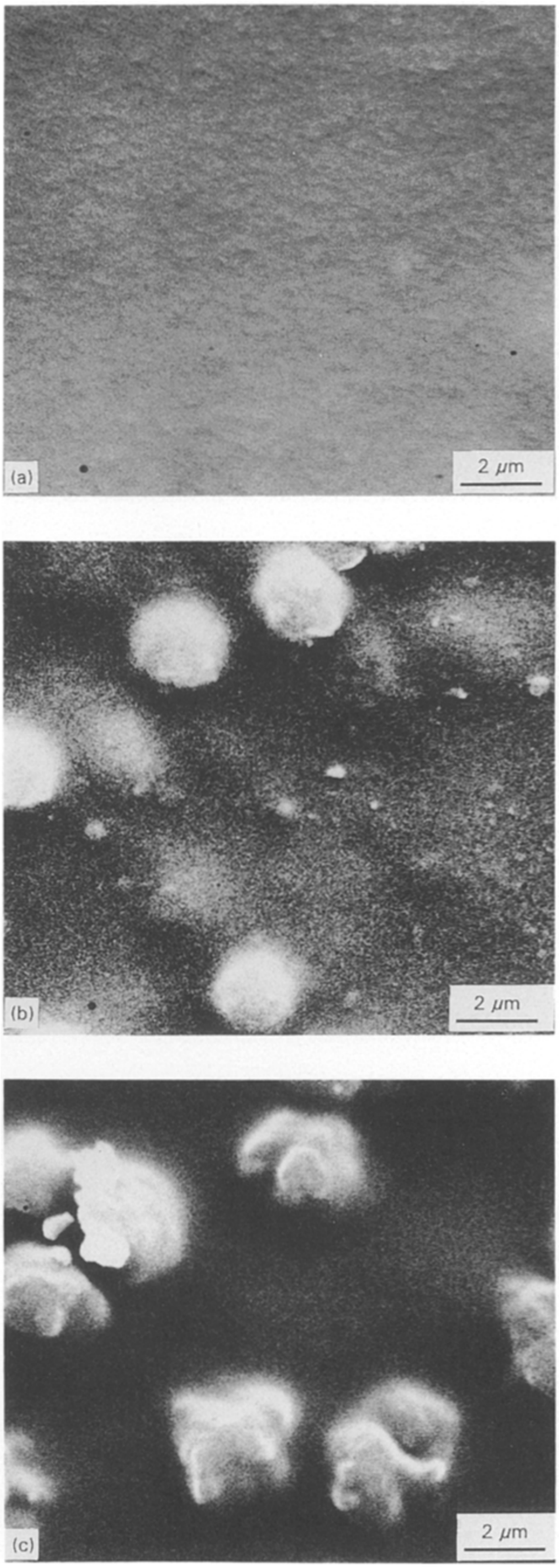


Figure 10 Scanning electron micrographs of (a) M_1(blends of PU with 0 wt % Nomex); (b), M_3(10 wt % Nomex); (c) M_5(20 wt % Nomex).

tensile strength, finally down to complete brittleness. The initial modulus and elongation were found progressively to increase as the Nomex content was increased and decreased, respectively. The elongation of

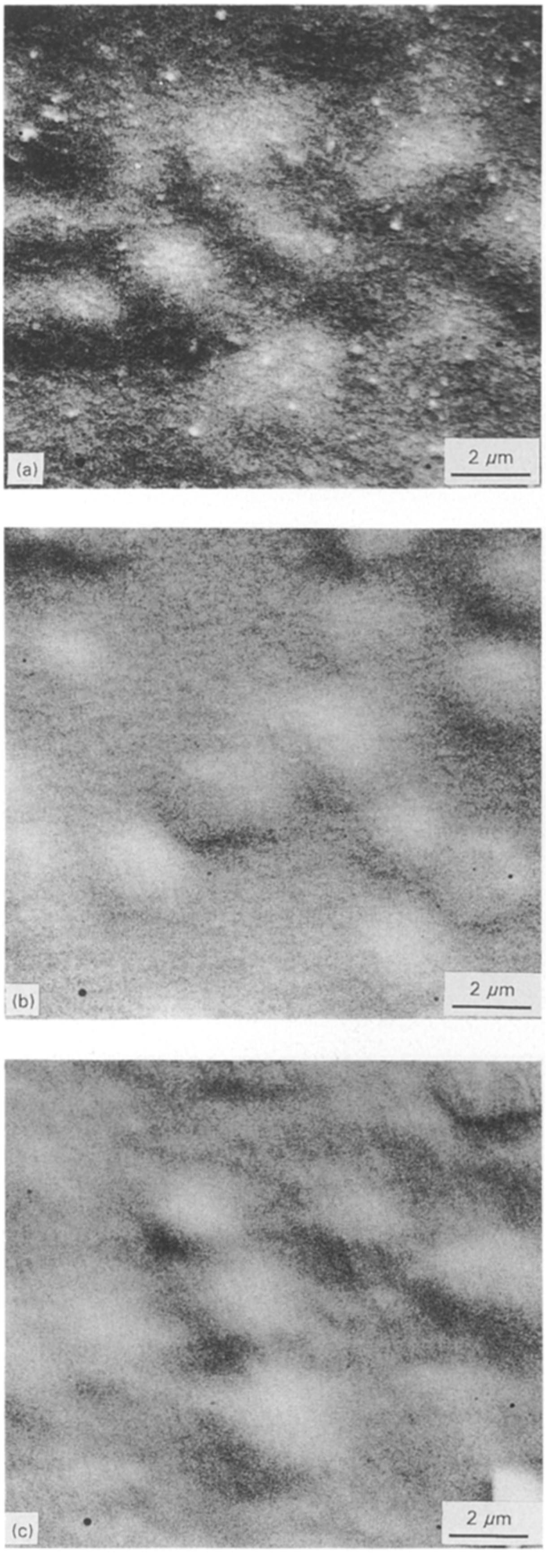


Figure 11 Scanning electron micrographs of (a) B_1(PU–1000–36 wt % Nomex); (b) B_2(PU–2000–25 wt % Nomex); (c) B_3(PU–2900–20 wt % Nomex).

TABLE IV Mechanical properties of polyblends and block copolyamides

Code	Nomex (wt%)	T_b (MPa)[a]	E_b (%)	M_i (MPa)
M_1	0	14.0	788	23.4
M_2	5	15.4	725	26.4
M_3	10	16.2	679	28.2
M_4	15	14.9	576	29.6
M_5	20	13.0	513	30.1
M_6	0	13.5	816	21.5
M_7	5	14.5	780	22.8
M_8	10	15.4	726	23.6
M_9	15	14.6	631	25.6
M_{10}	20	12.5	588	27.1
M_{11}	0	12.0	992	14.3
M_{12}	5	12.6	902	16.6
M_{13}	10	14.1	813	17.8
M_{14}	15	13.6	750	19.3
M_{15}	20	12.3	678	23.9
B_1	36	26.8	794	33.3
B_2	25	24.8	865	27.4
B_3	20	20.8	1040	23.6
N_m^b	100	70.0	11.2	9260.0

[a] $T_b/E_b/M_i$ = breaking tensile strength/elongation/initial modulus.
[b] From [10].

the blends was reduced because of the restraint of the wholly-rigid Nomex molecules, thus the yield strength was enhanced, but the ultimate elongation decreased. Mechanical properties of other polyblends (M_6–M_{15}) were similar to those of the PU–1000–BD/Nomex (M_1) polyblend series.

The effects on mechanical performance of incorporating the Nomex block segment in PU–2900–Nomex (B_3) are given in Fig. 12. It was found that the multiblock copolyamides had much better tensile strength and elongation than the polyblend with the same amount of Nomex. The multiblock copolyamides had better properties not ony due to the introduction of wholly-rigid units, which caused higher intramolecular stiffness, but also increase in intermolecular forces between the wholly-rigid Nomex and soft PTMG segments in the multiblock copolyamides.

4. Conclusions

Twelve PU/Nomex polyblends were prepared by physical blending and three multiblock copolyamides were synthesised by chemical extension. The reinforcement of polyurethane with wholly-rigid Nomex instead of conventional hard butyl segment proved successful. The multiblock copolyamides showed, for the same Nomex content, better mechanical properties than the polyblends. However, comparison of the dynamic mechanical properties of multiblock copolyamides with polyblends showed that the transition temperature, T_{gs}, in the lower temperature region of multiblock copolyamides was lower than in polyblends, and also the storage modulus, E', indicating the self-phase separation of the multiblock copolyamides in the soft segment.

With regard to morphology, the dispersed phase structure was observed in both polyblends and multiblock copolyamides. DSC analysis showed that wholly-rigid Nomex-reinforced polyurethane polyblends exhibited higher glass transition temperatures

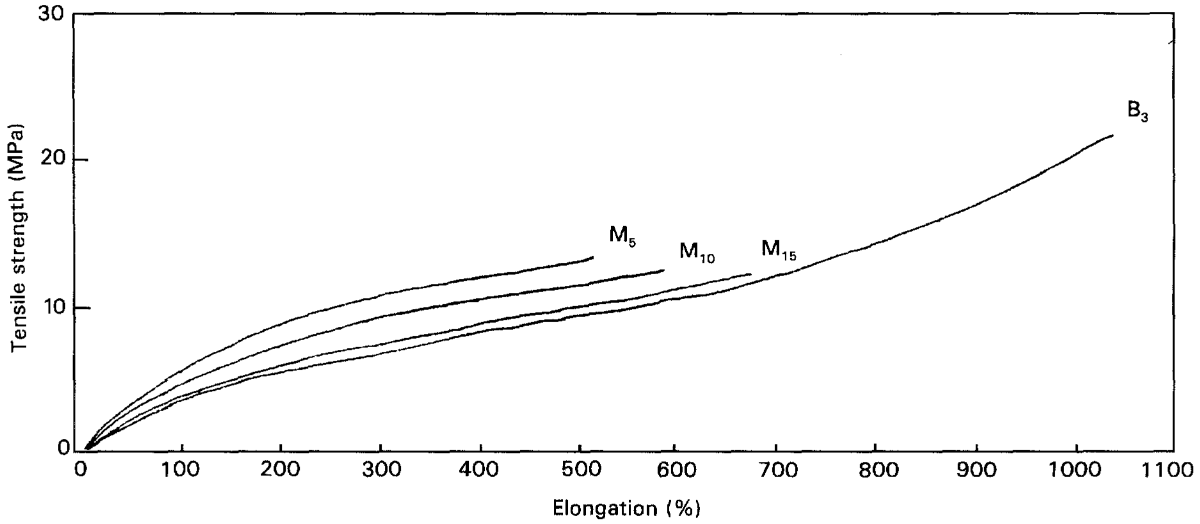


Figure 12 Stress–strain curves of polyblends and multiblock copolymides: M_5(20 wt % Nomex); M_{10}(20 wt % Nomex); M_{15}(20 wt % Nomex); B_3(20 wt % Nomex).

than that of polyurethane, which increased with increasing Nomex content. The T_{gh} and T_m of multiblock copolymides were even higher than those of polyblends.

X-ray diffraction could be used to identify the degree of stress-induced crystallization of polyurethane and multiblock copolyamides dependent on the segmental composition of the hard and soft segments, and also the degree of its stretching. The X-ray diffraction peak $2\theta = 20°$ corresponded to the soft PTMG segment for the (1 0 0) plane, although the X-ray diffraction peak $2\theta = 24°$ pertained to the diffraction peak of (0 1 0) plane of the soft PTMG segment. The optimum Nomex content in the polyurethane was considered to be 10 wt %.

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