Modification of Nylon-6 with Semi-rigid Poly (*p*-diphenylmethyl terephthalamide) Using MDI as a Chain Extender

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SYNOPSIS

The purpose of this study is to reinforce the flexible nylon-6 by using Poly (*p*-diphenyl methyl terephthalamide) (PMA) using MDI as a chain extender. Observation by scanning election 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, Tm, which is higher than that of nylon-6. The wide-angle X-ray diffraction pattern shows that nylon-6 has two diffraction peaks at $2\theta = 20°$ and 23.8°. However, the multiblock copolymer has only one peak at $2\theta = 20°$, indicating a different crystal structure of multiblock copolymers. The copolymers appears to have a significant reinforcing effect on the mechanical properties. © 1994 John Wiley & Sons, Inc.

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),[1-5] and poly (4,4′-diphenylsulfone terephthalamide) (PSA).[7-9] As shown in our previous paper,[6,7] the aliphatic nylon-6 was modified by the semirigid PSA, exhibiting better thermal and mechanical properties. In our studies, we used semirigid polyamide poly(*p*-diphenyl methyl terephalamide) (PMA) with (4,4′-diphenylene methane diisocyanate) (MDI) as a chain extender to reinforce the aliphatic nylon-6. The chemical structure of PMA is shown below.

The semirigid PMA has the same monoclinic crystal structure[10-13] as that of nylon-6.

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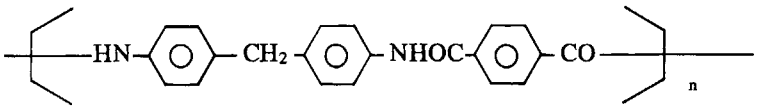
EXPERIMENTAL

Materials

Nylon-6 is made by Formosa Chemical and Fiber Corporation. Nylon-6 was first dissolved in formic acid and then poured into an excess amount of water. Samples are 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 $\overline{Mn}$ (21,500) of nylon-6 are obtained from the literature.[14]

ε-Caprolactam, 6-aminohexanoic acid, hexamethylene diamine, 4,4′-diphenylene methane diisocyanate (MDI), 4,4′-diaminodiphenyl methane (DDM), and terephthaloyl dichloride (TPC) were the products from Merck Co., and used as received.

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



PMA

Scheme 1

Preparation for Polyamides and Their Prepolymers

Low molecular weight diamine-terminated PMA is polymerized by low-temperature solution polymerization in NMP containing 5% LiCl at −10°C for 30 min. The reaction is shown below.

Low molecular weight diamine-terminated nylon-6 prepolymer was prepared by using an excess of hexamethylene diamine (HMDA) described in the literature.[15,16]

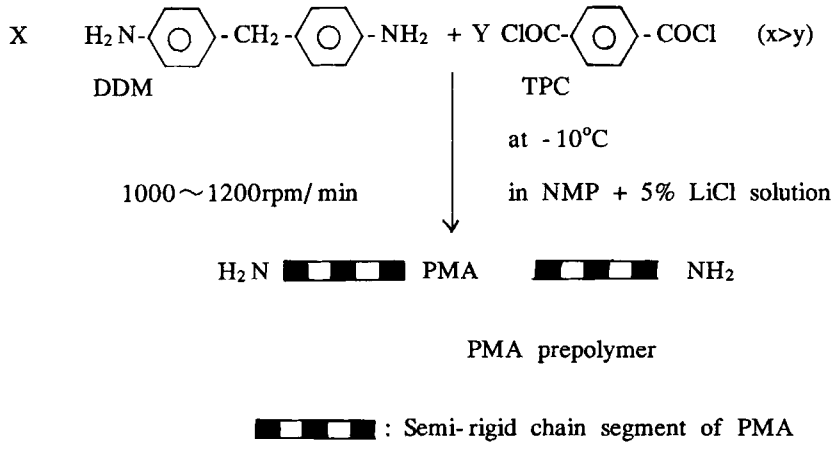
Synthesis of Nylon-6-MDI-PMA Block Copolymers

The copolymers were synthesized by reacting nylon-6 prepolymer and PMA prepolymer using MDI as a chain extender in the following procedure. The diamine-terminated nylon-6 prepolymer and PMA prepolymer in NMP + 5% LiCl are mixed and stirred vigorously in a nitrogen atmosphere system at 80°C for 30 min, then allowed to cool down and kept at 60°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 reactions are given below.

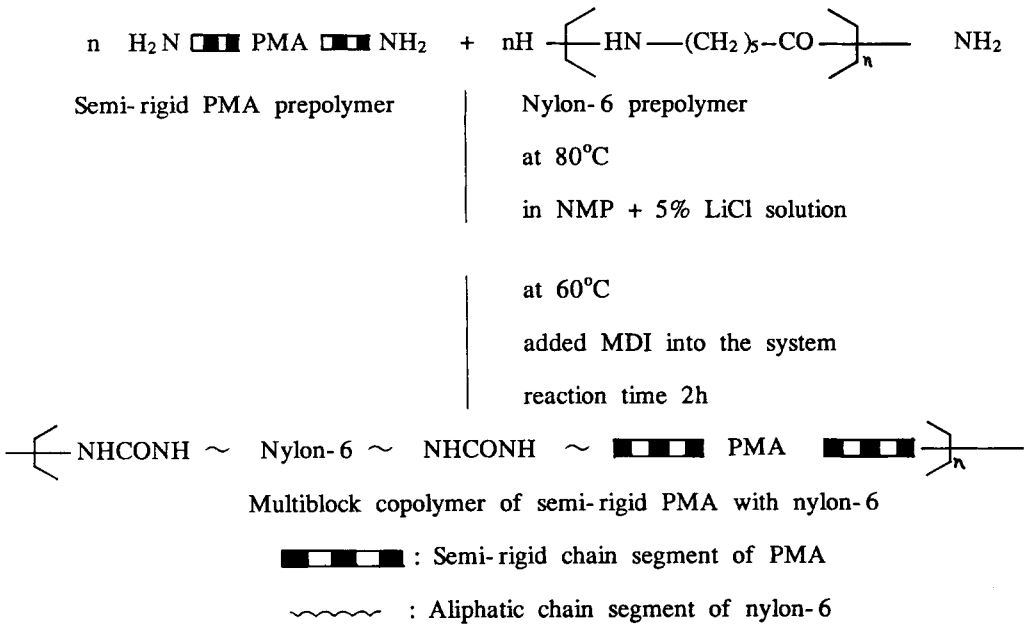
The various multiblock copolymers were prepared by the solution polymerization of nylon-6 prepolymer with different amounts (wt %) of semirigid PMA prepolymers. The inherent viscosities of the block copolymers are found to be greater than those of the prepolymers; that is, the block copolymers had a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

Measurements

Infrared spectra of homopolymers and copolymers were obtained using a Perkin Model 840 Type, over a range of 400–4000 cm^{-1}. The samples were films about 10 μm thick. Differential scanning calorimetry (DSC) was used to measure the temperature of crystallization, Tc, in a nitrogen atmosphere using a Du Pont model 9900 DSC; at a heating rate of 20°C/min, to obtain the glass temperature, Tg, and the melting temperature, Tm. Wide-angle X-ray photographs were taken with nickel-filtered C_uK_α radiation using Rigaku D/max-II Type X-ray diffractometer. A scanning electronic microscope,



Scheme 2



Scheme 3

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 δ, and dynamic modulus, E', with a RHEOVIBRON DDV-II-C. All stress-strain data were determined using an Instron 4201 Type testing instrument at an extension rate of 5 mm/min, and load cell with full load of 50 kg.

RESULTS AND DISCUSSION

Analysis of Infrared Spectra

Infrared spectra were obtained by using the technique of thin film. The transmission IR spectra of homopolymers and copolymers are shown in Figure 1, respectively. The IR spectra of nylon-6 (curve Ny) are characterized at 3,300 cm^{-1} (=N—H stretch-

Table I Characteristics of Multiblock Copolymers

Polymer	Nylon-6	10 Wt % PMA	15 Wt % PMA	20 Wt % PMA
η_{inh}[a]	0.87	0.95	1.05	1.03

[a] Measured at a concentration of 0.5 g dL/L in NMP + 5% LiCl at 30°C.

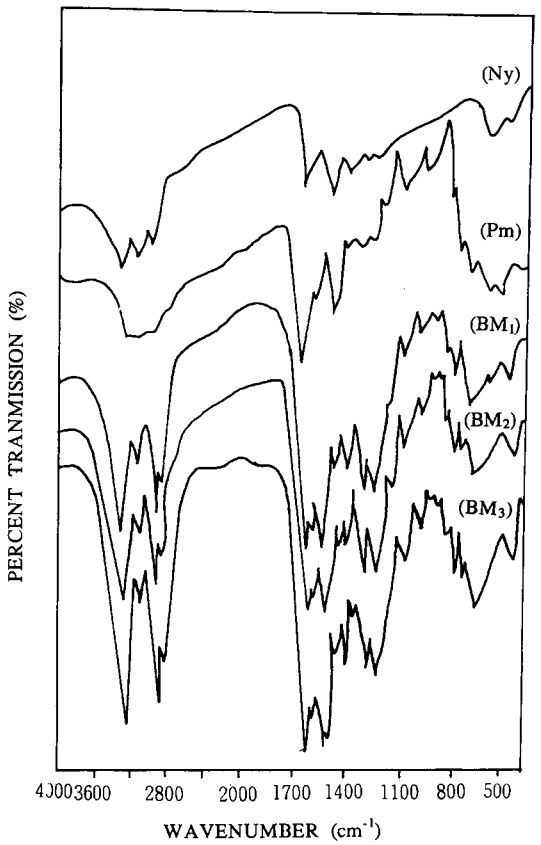


Figure 1 Infrared spectra of homo- and multiblock copolymer films: (Ny) nylon-6 homopolymer; (Pm) PMA homopolymer; (BM_1, BM_2, BM_3) multiblock copolymers of 10, 15, and 20 wt % PMA content.

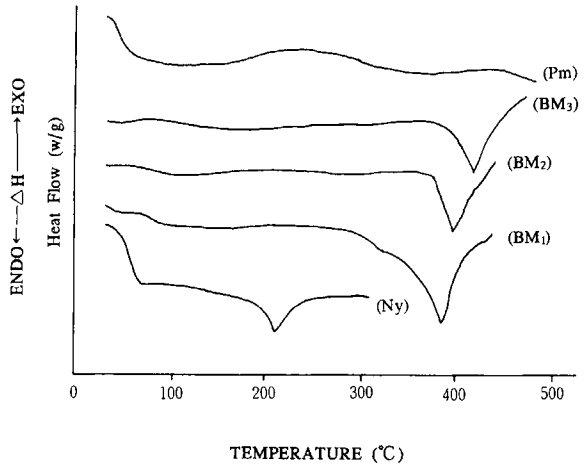


Figure 2 DSC plots of homo- and multiblock copolymer in nitrogen: (Ny), nylon-6 homopolymer; (Pm) PMA homopolymer; (BM_1, BM_2, BM_3) multiblock copolymers of 10, 15, and 20 wt % PMA Content.

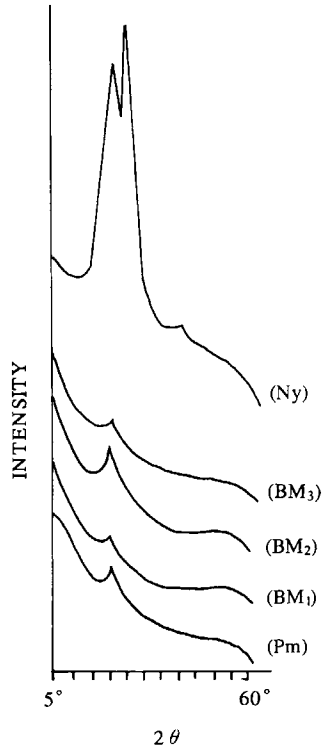


Figure 3 X-Ray diagrams of homo- and multiblock copolymer films: (Ny) nylon-6 homopolymer; (Pm) PMA homopolymer; (BM_1, BM_2, BM_3) multiblock copolymers of 10, 15, and 20 wt % PMA content.

ing vibration), 1,650 cm^{-1} (=C—O), 1,560 cm^{-1} (=N—H deformation), and 2,900 and 2,770 cm^{-1} (—CH_2- stretching vibration) absorptions; while the characteristic IR spectra of PMA (curve Pm) are shown at 1,530 cm^{-1} (—C_6H_4—CH_2—C_6H_4—), 1,660 cm^{-1} (—CONH—) and 1,100 cm^{-1}, 800 cm^{-1} (—C_6H_4— on parasubstituted) adsorptions. The nylon-6-PMA block copolymers (curve BM_1 to BM_3) show the characteristic absorptions of both nylon-6 and PMA. Noticeable are characteristic absorptions of the aliphatic —CH_2— at 2,900 cm^{-1}, 2,770 cm^{-1}, and at 1,530 cm^{-1} (—C_6H_4—CH_2—C_6H_4). In addition, nylon-6-PMA also shown are absorptions of —NHCONH— at 1,620–1,640 cm^{-1}, emanating from the reaction of the —NH_2— on the prepolymer with the —NCO group of the chain extender.

Thermal Properties of Block Copolymers

Polymers with aromatic ring structure could contribute to their thermal stability. In this study, the presence of aromatic PMA in nylon-6 could be expected to provide better thermal properties. The thermal behavior of homopolymers and block copolymers measured by DSC is shown in Figure 2 and Table II. The results show that the glass transition temperature, Tg, and the melting point, Tm, of the block copolymers have increased compared with that of nylon-6. Because the transition temperature could indicate the behavior of molecular motion within the polymer, it could be used as a clue to identify the phase separation, or the compatibility. The glass transition temperature, Tg, of block copolymers shows only one peak, therefore, a compatible state of semi-rigid PMA with nylon-6 is pos-

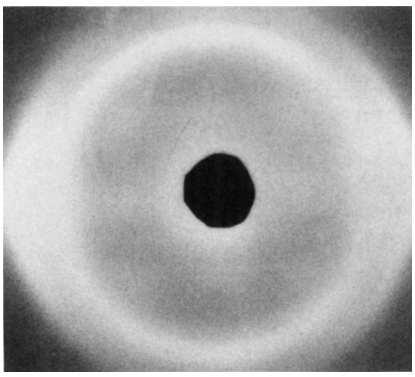
Table II Tg and Tm Measured by D. S. C Analysis

Polymer	Nylon-6	PMA	10 Wt % PMA	15 Wt % PMA	20 Wt % PMA
Tg (°C)	67	300	87	96	102
Tm (°C)	215	> 510	386	397	412

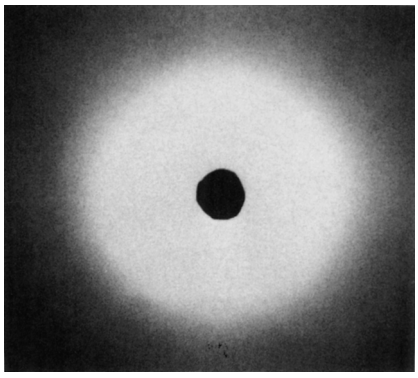
Table III D-Spacing and Crystallite Size of Nylon-6 and Multiblock Copolymers

Code	Polymer Form	d(200) A°	d(002, 202) A°	L(200) A°	L(002, 202) A°
Ny	Nylon-6	4.373	3.729	132.0	127
BM_1	Multiblock 10 wt %	4.306	—	122.7	—
BM_2	Multiblock 15 wt %	4.369	—	81.8	—
BM_3	Multiblock 20 wt %	4.456	—	75.6	—

sible in the block copolymers. From the analysis of DSC results, the melting temperature of the block copolymers is expected to rise with increasing PMA content. This is the result of the strong hydrogen-bonding connecting the nylon molecule and the nearby urea group, and the immobilization of immobile structure of MDI. Therefore, the block copolymers exhibit a more regular and wholly crystal structure.



(a) Nylon-6



(b) BM_1

Figure 4 WAXD patterns of nylon-6 and multiblock copolymer: (a) nylon-6; (b) multiblock copolymer (BM_1: PMA content of 10 wt %).

Wide-Angle X-Ray Diffraction

From the WAXS diffraction patterns in Figures 3 and 4, we know that nylon-6 has two diffraction peaks at $2\theta = 20°$ and 23.8°. However, the block copolymer has only one peak at $2\theta = 20°$. These results evidently indicate a new structure of the block copolymers is formed, that is, the $\alpha(200)$ plane of nylon-6-MDI-PMA block copolymer in a structure of nylon-6 forms a new crystal structure.

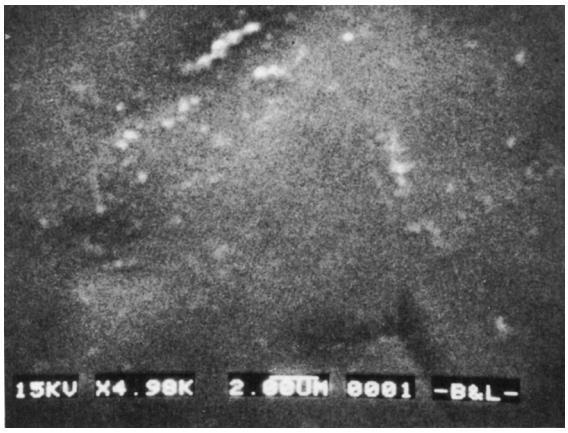
The data in Table III, though, indicate that the d-spacings of nylon-6 and block copolymers are similar, but the crystallite sizes differ from each other. The crystallite sizes of block copolymers is smaller than that of nylon-6.

Morphological Observation

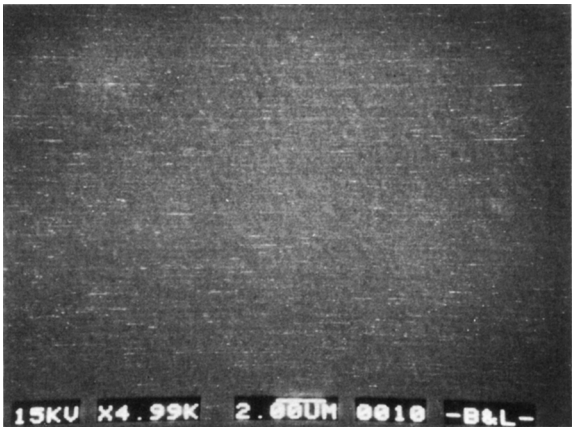
Scanning electron microscopy (SEM) was used to observe the microstructure of block copolymers. The micrographs in Figure 5 show the uniform surface structure of the block copolymers, resulting from covalent molecular chain displaying homogeneous morphology in block copolymers.

Mechanical Properties of Copolymers

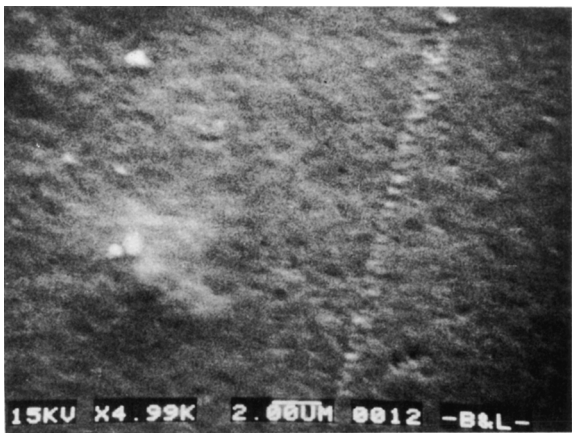
The mechanical properties of block copolymers are shown in Table IV and Figure 6. The tensile strength, Tb, and the initial modulus, Mi, of block copolymers are much better than those of nylon-6; 15% PMA content of the block copolymers is optimum, but the elongation of block copolymers is reduced. Obviously, nylon-6 is a ductile material originally, but after modification will become a stronger and more brittle material. The ordered block co-



(a) PMA 10wt%



(b) PMA 15wt%



(c) PMA 20wt%

Figure 5 SEMs of (a) multiblock copolymer of 10 wt % PMA content; (b) PMA 15 wt %; (c) PMA 20 wt %.

Table IV Mechanical Properties of Nylon-6 and Multiblock Copolymers

Code	Polymer	Tb (MPa)	Eb (%)	Mi (GPa)
Ny	Nylon-6	45.190	44.0	0.886
BM_1	Multiblock 10 wt %	62.935	16.7	1.908
BM_2	Multiblock 15 wt %	74.531	16.1	2.155
BM_3	Multiblock 20 wt %	62.462	12.5	1.911

Tb/Eb/Mi = Breaking tensile strength/elongation/initial modulus.

polymers have better properties, not only because of the introduction of semirigid units, which caused a higher intramolecular stiffness, but also because of the increase in the intermolecular forces between

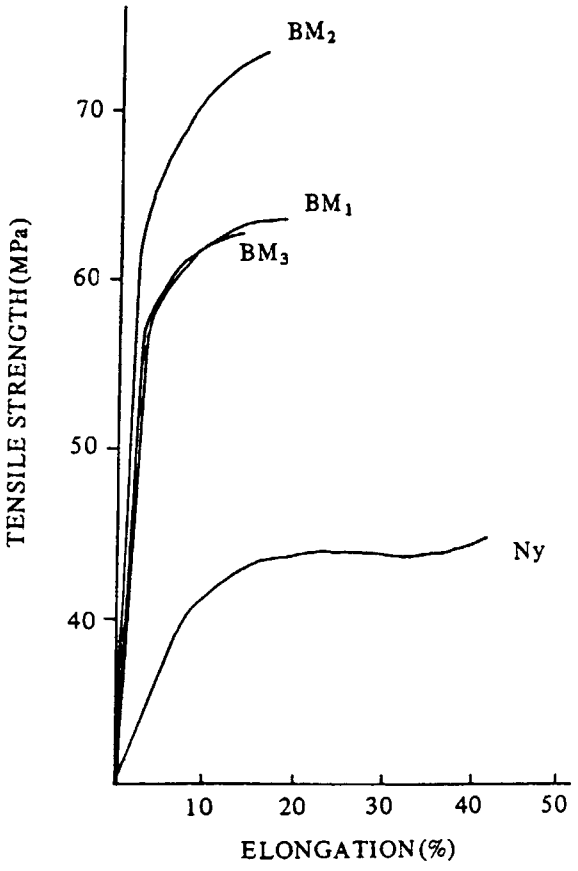


Figure 6 Stress–strain curves for multiblock copolymer: (Ny) nylon-6; (BM_1) PMA content of 10 wt %; (BM_2) PMA content of 15 wt %; (BM_3) PMA content of 20 wt %.

the polymer chains; thus forming a more uniform and compatible structure.

The loss tangent, tan δ, and tensile storage modulus, E', of nylon-6 and block copolymers are presented in Figures 7 and 8, respectively. Figure 7 shows that the glass transition temperature, Tg, of block copolymers is higher than that of nylon-6 homopolymer, and rises as the content of PMA increases. This results from the resonance-planarity of the aromatic structure which will decrease the free rotation and flexibility of molecular chain. Although the greater the amount of PMA, the greater the aromatic structure of the molecular main chain, Table I shows that viscosity average molecular weight will decrease with the increasing PMA content. Because of these two factors, the glass temperature, Tg, of 20 wt % PMA will be slightly higher than that of 15 wt % PMA.

Figure 8, shows that mechanical performance is altered in the same way as the tensile test, and will be when 15 wt % PMA is add.

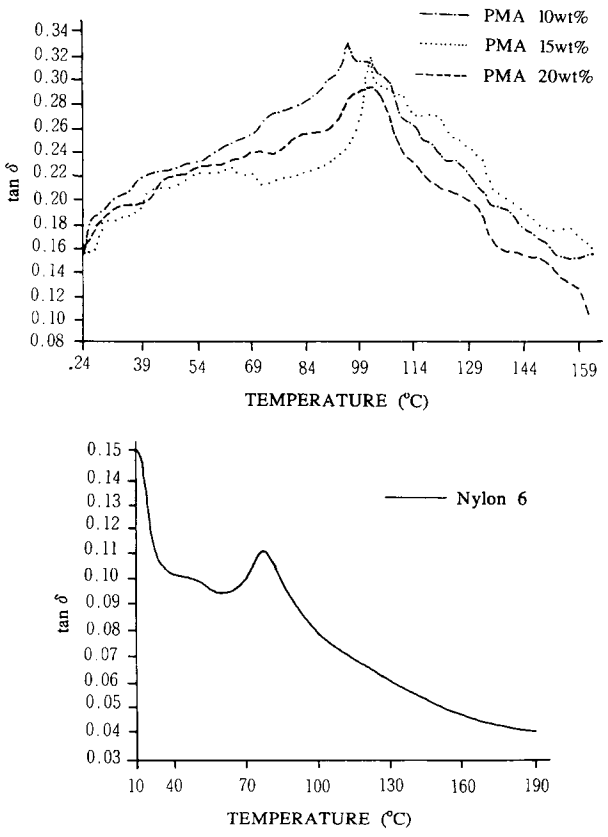


Figure 7 Plots of tan δ versus temperature for nylon-6 and its multiblock copolyamides.

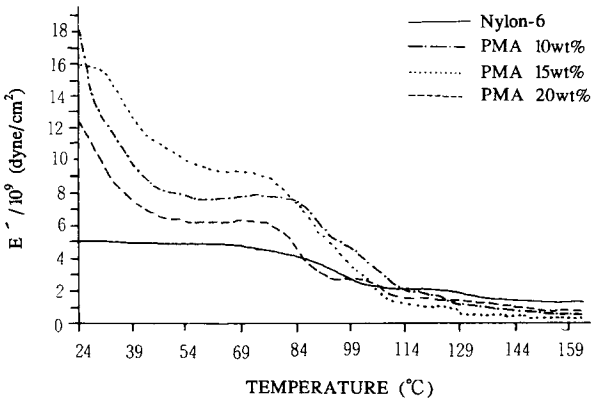


Figure 8 Plots of E' versus temperature for nylon-6 and its multiblock copolymers.

CONCLUSIONS

Three nylon-6-PMA block copolymers were synthesized by chemical extension using MDI as a chain extender. The reinforcement of nylon-6 with semirigid PMA 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 semirigid PMA reinforced nylon-6 forming copolymers exhibit both a higher glass transition and melting temperature than those of nylon-6 homopolymer; these will increase with the addition of PMA.

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

From measurement of mechanical properties, the mechanical properties of block copolymer were found to be excellent compared with those of nylon-6 homopolymer, but 15 wt % PMA was the best. Therefore, the optimum PMA content in nylon-6 is suggested to be 15 wt %.

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