Synthesis and Characterization of the Feed Ratio of Polyethylene Oxide (0 ~ 10 Wt % PEO) in the Nylon-6/PEO Copolymer System

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ABSTRACT: In this work, we have synthesis nylon-6/polyethylene oxide (PEO) copolymer system based on feed ratio of PEO (0~ 10 wt %) through condensation polymerization in a pilot scale. The structure of copolymer was confirmed by Fourier transform infrared (FTIR) spectroscopy and verified by ^{1}H nuclear magnetic resonance (^{1}HNMR). The thermal properties were investigated by differential scanning calorimetry (DSC) and indicated both melting temperature (T_m) and cold crystallization temperature (T_c) appearing unapparent decreased while increased PEO content in copolymers. The incorporation of PEO into the nylon-6 chain reduced its tensile strength, modulus, and heat distortion temperature (HDT). The notched Izod impact strength of and ductility of the copolymers improved significantly as the PEO content was increased. The plasticizing effect was caused by the soft segments from PEO, which increases the mobility of the molecular chain in the copolymers. The results of mechanical tests agree closely with dynamic mechanical analysis (DMA) measurements. A rheological investigation revealed that neat nylon-6 and its copolymer displayed similar behavior. The crystalline structure was examined by wide-angle X-ray diffraction (WAXD). The results demonstrate that the addition of a little PEO altered the crystallization from the α form to the γ form, mainly owing to the breaking parts of the original H-bonds by the incorporation of ether groups. A mechanism of interaction between the amide and the ether group in nylon-6/PEO copolymers is proposed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 796–806, 2012

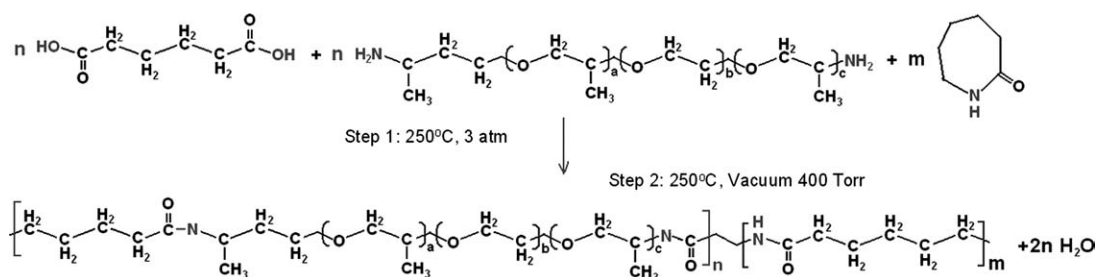**Key words:** copolymer; polyethylene oxide; nylon-6; crystallinity

INTRODUCTION

Nylon-6 is synthesized from caprolactam. The structural units of nylon-6 are linked by amide, -NH-CO-, group. Neighboring segments in nylon-6 attract to each other by intermolecular forces, namely the hydrogen bonds. Nylon-6, characterized by its ease of processing, dominates the thermoplastic industries and is widely used as an engineering plastic.[1] Its use in food packaging as part of a multilayer, produced by coextrusion has recently become promising.[2,3] Another related development includes the formation of fibers with special features of softness, abrasion resistance, light weight, and high strength. Nylon-6 was one of the first synthetic fibers to be developed and is still exploited in numerous industrial products.[4] Under specific conditions, nylon-6 easily becomes brittle, showing poor impact, and stiffness properties. The literature includes many approaches for increasing the toughness of nylon-6, focusing mainly on the introduction of a soft, flexible polymer or hydrocarbon elastomer into the nylon-6 matrix by either grafting or blending. Related research has been carried out on maleated styrene/butylenes/styrene block copolymer,[5] malic anhydride maleated ethylene/propylene polymer,[6,7] epoxy-functionalized acrylonitrile-butadiene-styrene,[8–10] ethylene-vinyl acetate copolymer with the ethylene-acrylic acid polymer,[11,12] epoxidized or modified robber,[13–15] nylon-6/polycarbonate blends,[16] polyimide/nylon-6 block copolymers,[17] terminal anhydride functionalized polystyrene/nylon-6 blend,[18,19] and 2, 6-dimethyl-1,4-phylene oxides.[20] Nanotechnology shows promising results for nylon-6 composite recently. The toughness can be improved by nylon-6/silica and nylon-6/clay composites when the nanoparticle acts as a nucleating agent.[21,22] Moreover, the carbon nanotube remarkably improve mechanical and electric properties of nylon-6.[23,24] However, because of the complexity of the required process and for reasons of price, few modifications are made on a commercial or industrial scale. Therefore, this work provides a simple, economical

Scheme 1 Synthesis of nylon-6/PEO copolymer.

approach for not only enhancing the impact properties of nylon-6 but also ensuring ease of postprocessing.

PEO has many applications. Poly(ethylene oxide) diamine (PEODA) can act as a substitute for modified nyon-6. Hence a soft segment of PEO is introduced into nylon-6 to form copolymer with improved toughness.[25–27] PEO supplies flexible segments and hydrophilic moieties, which enable the nylon-6/PEO fiber to perform like a natural fiber,[28] making it an important constituent of biodegradable material by chain hydrolysis.[29] However investigation of the basic properties of nylon-6/PEO copolymer, including its rheology, thermal properties, crystalline structure, and mechanical properties are lacking.

In this work, various proportions of PEO (wt % PEO) were introduced into nylon-6/PEO copolymers through condensation in a pilot scale. The chemical change in the copolymers was examined using FTIR spectroscopy and identified by ^{1}HNMR spectroscopy. The thermal properties, obtained using DSC and DMA included the T_m, T_c, and glass transition temperature (T_g). The rheology was examined using a capillary rheomete. The crystalline structure was elucidated by WAXD. The results indicated that the addition of a little PEO altered the crystallinity from the α form to the γ form, mainly by breaking up parts of the original H-bonds by the incorporation of ether groups. Finally, the mechanical properties of copolymers were investigated by tensile tests, notched Izod impact strength and HDT. The mechanism of interaction between the amide and the ether group in the copolymers is proposed; PEO bonding to C=O group was responsible for the breaking of the original hydrogen bond. The intermolecular hydrogen groups transformed from the pair of C=O, N—H to the pair of C—O—C, N—H was described. Meanwhile, the results from mechanical properties illustrated PEO also provide plasticizing effect caused by the soft segments, which increases the mobility of the molecular chain in the copolymers.

EXPERIMENTAL

Material

Caprolactam (CPL) was purchased from DSM. PEODA was obtained from Huntsman; its molecular weight was ~ 2000. Adipic acid (AA) was supplied by BASF. The flake CPL, PEODA, and stoichiometric AA with a small amount of water (about 4 wt %) were charged into an autoclave (300 L).

Synthesis of nylon-6/poly(ethylene oxide) copolymer

The reactor was purged by nitrogen four times before heating was begun. The temperature was raised to 250°C before the agitator was switched on. To initiate the hydrolytic polymerization of CPL, the pressure was set to 3 atm to prevent the water from evaporating in the reactor, in which the ring opening reaction was carried out. After 3 h, the pressure was slowly returned to atmosphere and the water evaporated. The vacuum system was turned on to maintain the pressure of around 400 Torr. Scheme 1 describes the chemical reaction that then occurred. The molecular weight of copolymer was increased rapidly in the vacuum condition, reaching the desired molecular value after 2 or 3 h. The nylon-6/PEO copolymer melt was then cooled and pelletized. The pellets were immersed in hot water for 20 h to extract the unreacted CPL and oligomer, which contributed ~ 10% of the CPL feeding weight. After the washing procedure was completed, the pellets were dried in vacuum at 110°C for 20 h and stored in a special package to prevent leakage. Table I presents all of the recipes for constituents of the copolymers.

The feed ratio is PEO content to the amount of copolymer before extraction. The theoretical ratio is the PEO content to the amount of copolymer after extraction. Equations (1) and (2) present their relationship. (A is the feeding weight of the CPL; B is the feeding weight of PEODA; C is the feeding weight of AA.)

$$\text{Feed ratio} = \frac{B}{A + B + C} \qquad (1)$$

$$\text{Theoretical final ratio} = \frac{B}{A \times 0.9 + B + C} \qquad (2)$$

Preparation of sample

All copolymer sheets were obtained using a compression mold at 230°C. To prevent oxidation during

TABLE I
Formulation of Nylon-6/PEO Copolymers

wt % PEO	CPL (kg)	PEODA (kg)	AA (kg)	Water (kg)	PEO content before extraction (Feed ratio %)	PEO content after extraction (Theoretical final ratio %)
0	100	0	0	4	0	0
2	96	1.77	0.129	4	1.81	2
4	92	3.46	0.253	4	3.61	4
6	88	5.08	0.371	4	5.44	6
8	84	6.62	0.483	4	7.27	8
10	80	8.07	0.589	4	9.10	10

the cooling process, the rate of cooling obtained using cooling water was increased immediately after the sheets were formed. The sheets were cut in specific shapes for specific tests, which included DMA, WAXD, and mechanical property testing.

Characterization

Structure

FTIR spectra of the copolymers were carried out using NICOLET 380 spectrometer, with 64 scans at a resolution of 4 cm^{-1}, using the attenuated total reflectance (ATR) method.

^{1}HNMR, Bruker Avance DRX400 at 400 MHz, was utilized to identify the chemical structure of the copolymers. Deterated trifluoro acetic acid (TFA) was used as a solvent. The reference compound was 100 mg Cholac/mL deuterated chloroform (CDCL$_3$) + 0.5% tetramethylsilane (TMS).

Determination of molecular weight

To estimate the molecular weight, amino-end-group analysis was performed. About 0.5 g of the sample was placed in a 100 mL titration cup, and a 50 mL of phenol/methanol mixture was added. The titration cup was stirred until the sample was completely dissolved. The solution was titrated with 0.05N standard perchloric acid (HClO$_4$). The blank, 50 mL of a mixed solvent, was titrated in the same way. The concentration of amino end groups was calculated as using eq. (3). (A denotes the volume of HClO$_4$, used as the solution, and is given in mL; B is the volume of HClO$_4$ used as blank, given in mL; N is the equivalent concentration of the HClO$_4$, in eq/L and W is the mass of the sample, g.).

$$[\text{---NH2}]\text{mEq/kg} = \frac{(A - B) \times N \times 1000}{W} \quad (3)$$

Thermal properties

The thermal stability of the copolymer was determined using a thermogravimetric (TGA, TA Q-500).

Samples were heated to 700°C at a rate of 10°C/min under nitrogen blanketing. The T_m was measured by DSC (TA Q-100) at a heating rate/cooling rate of 10°C/min from 30 to 300°C, which temperature was held for 5 min before cooling to 30°C.

Dynamic mechanical analysis

The dynamic mechanical analysis of the copolymers was investigated by DMA (PERKIN 7e). The specimens had a length, width, and thickness of 12, 5, and 1 mm, respectively. Their temperature was adjusted from 20 to 150°C at a scan rate of 5°C/min. The static force was kept at 70 mN; the dynamic force was set to 60 mN. The frequency used was 1 Hz and the amplitude was 5 μm.

Capillary flow viscometer

The apparent melt viscosities at various shear rates were measured using a capillary rheometer with a length/diameter ratio of 10 (GOTTFERT RHEO-GRAPH 25) at 270°C. The shear rate was adjusted from 10^3 to 10^4 s^{-1}.

Moisture absorptions

The moisture absorption of the sample depended on the chip size, ambient temperature, relative humidity, and the type of polymer. In this study, the pellets had a diameter, length and width of 2.3 mm, 2.5 mm, and 2.3 mm, respectively. The conditions were a controlled temperature and relative humidity of 25°C and 65%, respectively. Each prepared copolymer weighed around 100 g. The moisture regain (MR) was obtained using eq. (4). (A is the mass of the dried sample, and B is the mass of the sample after treatment with moisture.)

$$\text{Moisture regain} = \frac{B - A}{A} \quad (4)$$

Wide-angle X-ray diffraction

WAXD was carried out at room temperature. X-ray was generated as Cu Kα radiation (λ = 0.154 nm) at
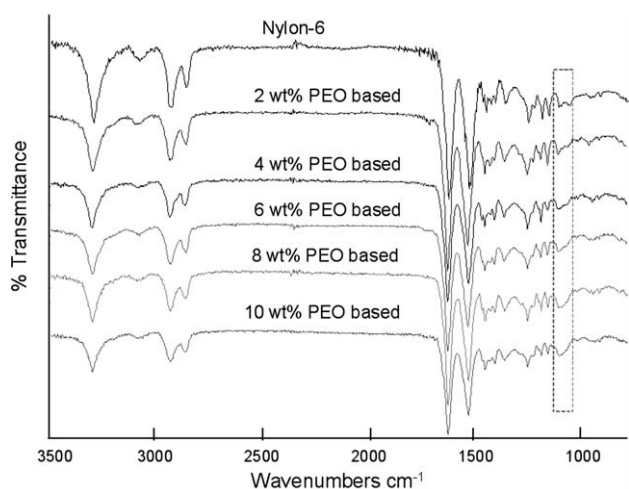
Figure 1 FTIR spectra of nylon-6/PEO copolymers.

45 kV and 40 mA (Panalytical X'Pert Pro PW3040/60). The scanning 2θ angle was from 10 to 60°.

Mechanical properties

The notched Izod impact strength, ASTM D256, was measured using INSTRON type 5567. The tensile strength, ASTM638, was determined using ZWICK type 5567. The length, width, and thickness of specimens were 127 mm, 12.7 mm, and 3.2 mm, respectively. The speed of tensile strength in the test was 5 mm/min at room temperature. Each datum was obtained as an average of five specimens. The heat distortion temperature (HDT) test, ASTMD-648, 3.15 (width) $\times$ 13.13 (height) mm, was performed using GT-HV 2000. The stress was kept 0.455 MPa and was heated at 2°C/min until the specimen was deflected by 0.25 mm.

RESULTS AND DISCUSSION

Structure conformation (FTIR, ^{1}HNMR)

Figure 1 presents the distinctive absorption bands of nylon-6. The bands at 3300, 3215, and 3085 cm^{-1} are associated with NH stretch vibrations. The broad band at 1640 cm^{-1} corresponds to the stretching vibration of the C=O bond of the amide group, and that at 1545cm^{-1} corresponds to the stretching vibration of the C—N bond of the amide group. The C—H stretching vibrations occur at 2860 and 2930 cm^{-1}. The IR spectra results verify the characterization of nylon-6. Unlike neat nylon-6, the specimens yielded little absorption bands at 1120 $\sim$ 1090 cm^{-1}, which were associated with the stretching vibration of C—O—C. However, many signals overlap each other, making distinguishing among them difficult.[30,31] Consequently, the PEO ratio in nylon-6/PEO copolymers cannot be easily calculated from IR spectrum.

To determine precisely the structure of the copolymer, ^{1}HNMR spectroscopy was utilized both to identify the copolymer and to estimate the weight fraction of PEO.[1]H. Nylon-6, typically exhibits a chemical shift at below 3.6 ppm in the ^{1}HNMR spectra. The chemical shifts of ether are at 3.9 ppm.[30] Figure 2 shows the characteristic peaks of the nylon-6/PEO copolymers in the ^{1}HNMR spectra. The PEO content in the prepared copolymers is determined by comparing area under the peak at 3.9 ppm for
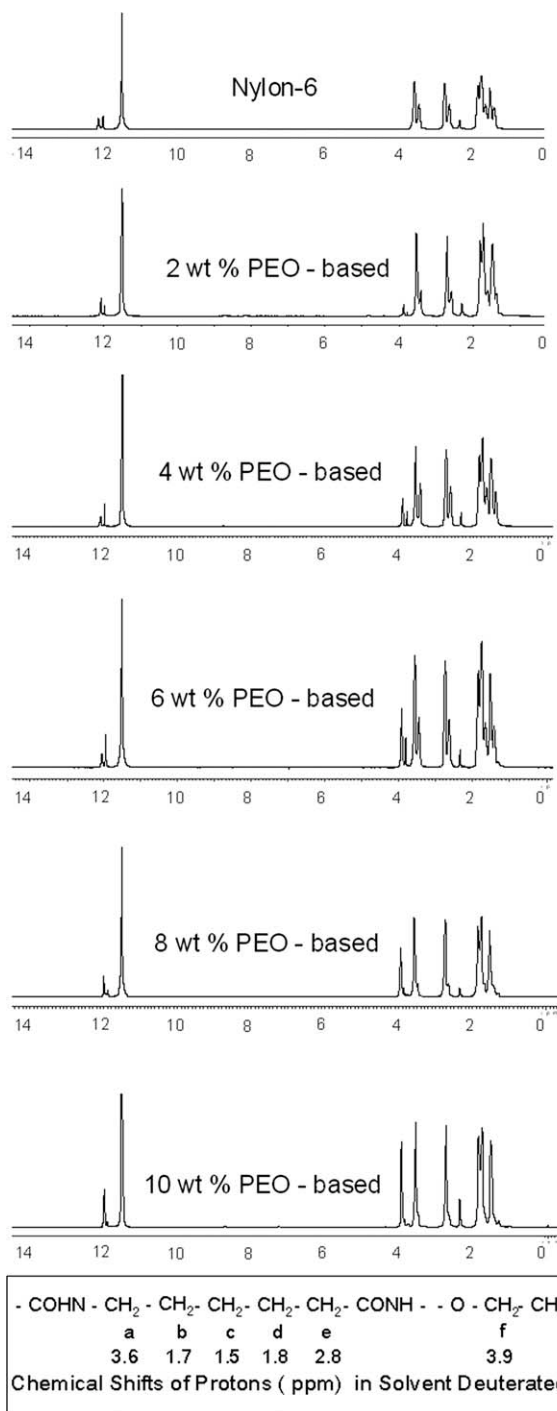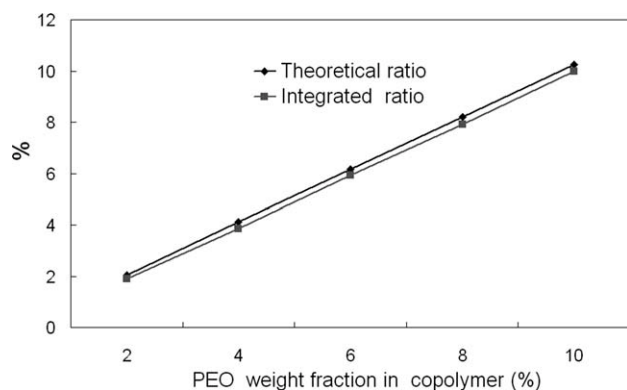

-COHN-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CONH--	-O-CH$_2$-CH$_2$-O-

Figure 2 ^{1}HNMR spectra of nylon-6/PEO copolymers.

Figure 3 Theoretical ratio (top) and integrated ratio (bottom) in ^{1}HNMR spectra for nylon-6/PEO copolymers.

ether and that below 3.6 ppm for nylon-6. Equation (5) employs the theoretical proportion of PEO in copolymers:

$$\frac{(\mathrm{CH_2CH_2O})n}{\text{ratio}} =$$

$$\frac{(\mathrm{CH_2CH_2O})n \text{ wt \%} \ \frac{4}{44}}{(\mathrm{CH_2CH_2O})n \text{ wt \%} \times \frac{4}{44} + (\text{Nylon-6 wt \%}) \times \frac{10}{113}} \quad (5)$$

The integrated areas under ^{1}HNMR peaks were similar to theoretical proportion. The results reveal that the ratio of contents in this experiment is consistent with the theoretical ratio. Figure 3 compares the theoretical ratio and that determined by integration of the peaks. Notably, the complicated equilibrium among the unreacted CPL, cyclic oligomers, and the polymer was responsible for the slight deviation.

Determination of molecular weight

Equation (6) yields the average molecular size:

$$\frac{\text{Number average}}{\text{molecular weight}} = \frac{1}{[\overline{\quad}\text{NH2}]\text{mEq/kg}} \times 10^6 \quad (6)$$

Table II summarizes the various molecular weights of the prepared copolymers, determined by end group analysis. The average molecular weights of

TABLE II
Molecular Weight Characterization by Amino End Group Analysis

wt % PEO	Amino end group analysis (meq/kg)	Mn from Amino end group analysis
0	52	19,231
2	55	18,182
4	49	20,408
6	48	20,833
8	45	23,256
10	42	22,727
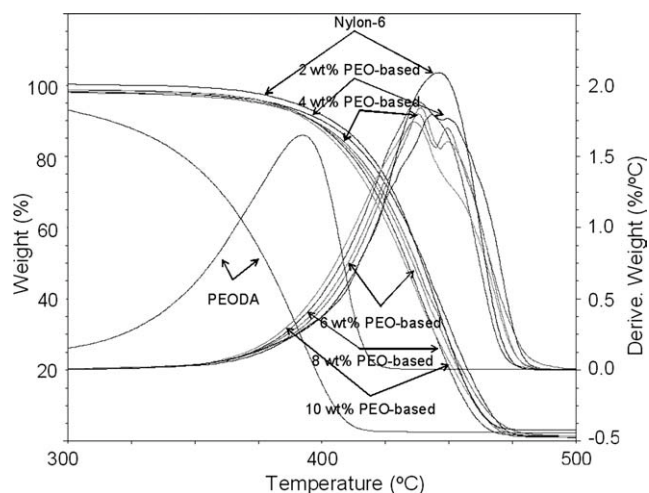
Figure 4 TGA curves of nylon-6 and copolymers with various PEO content.

the copolymers, regardless of the PEO content, were ~ 20,000. Hence, the molecular weight of these copolymers exceeded the critical value, 16,000, indicating that the synthesized copolymers were sufficiently large enough to form entanglements and to have stable physical properties like neat nylon-6.

Thermal properties (TGA, DSC)

Figure 4 presents the thermal decomposition of various copolymers from TGA. PEODA has poor heat stability because its interchain force is weak. It has no polar group. In contrast, in nylon-6 and nylon-6/PEO copolymers, most of the segments attract neighboring segments by hydrogen bonds, enhancing thermal stability. The TGA results reveal that all of the nylon-6/PEO copolymers underwent similar thermal decomposition process. The similarity of degradation behaviors regardless of PEO content may be attributable to the covalent bonding C—C and C—O within the nylon-6 matrix. Typical covalent bonding energies of C—C and C—O are 83 and 84 kcal/mol, respectively,.[32] These covalent bonds have almost the same energy. Therefore, the thermal decomposition trace of the copolymer was similar to that of nylon-6. The decomposition temperatures measured at 5% weight loss and 50% weight loss vary from 379 to 389°C and from 430 to 440°C, respectively. However, as expected, both temperatures declined as the PEO content increased, reflecting defects in the crystal structure. Meanwhile, a considerable decrease in maximum weight loss temperature as PEO involved was found, shifting from 446°C of neat nylon-6 to 436°C of 10 wt % nylon-6/PEO copolymer. Table III summarizes the TGA results obtained from nylon-6/PEO copolymers.

DSC data on the copolymers demonstrate that their T_m values do not change significantly from that

wt % PEO	5% weight loss/temp (°C)	50% weight loss/temp (°C)	Temp at maximum wt loss (°C)
0	388.8	439.5	446.1
2	380.5	440.3	443.4
4	374.8	437.2	437.8
6	376.7	435.8	438.9
8	379.9	433.8	437.9
10	379.0	432.6	436.3
100	285.1	378.4	392.4

of neat nylon-6 as the PEO content increases to 6 wt % [Fig. 5(a)]. Mateva et al. discovered that the T_m of nylon-6/polyisoprene does not change apparently with polyisoprene content up to 10 wt %. They proposed that polyisoprene segments are located in the amorphous region.[25] Incorporating small amount of PEO into nylon-6 does not seriously disturb the degree of crystallinity. The PEO chain is well known for its flexibility and lack of bulkiness. Most of the PEO segments are reasonably assumed to be squeezed in an amorphous phase, because of their flexibility. Hence, the T_m was maintained as the PEO content increased. However, the results show a decrease in melting temperature with increasing PEO content up to 8 wt %, indicating that the inclusion of the PEO decreased crystallinity in the copolymers. The cooling DSC scans in Figure 5(b) yields similar results. The T_c does not show pronounced shift until up to 8 wt %. However, the incorporation of the PEO decreases the heat of crystallinity while increasing the PEO content. At 8 wt % PEO copolymer, the T_m and the enthalpy of fusion are 219.4°C and 50.7 J/g, respectively. These values are around 1.8°C and the 7.1 J/g lower, respectively, than those of neat nylon-6. Furthermore, the crystalline peak becomes broader with increasing PEO content, suggesting that the PEO segments either reduce the degree of crystallinity or alter the crystalline phase. To elucidate the crystalline structure of the copolymers, WAXD was carried out. The results will be presented in a later section.
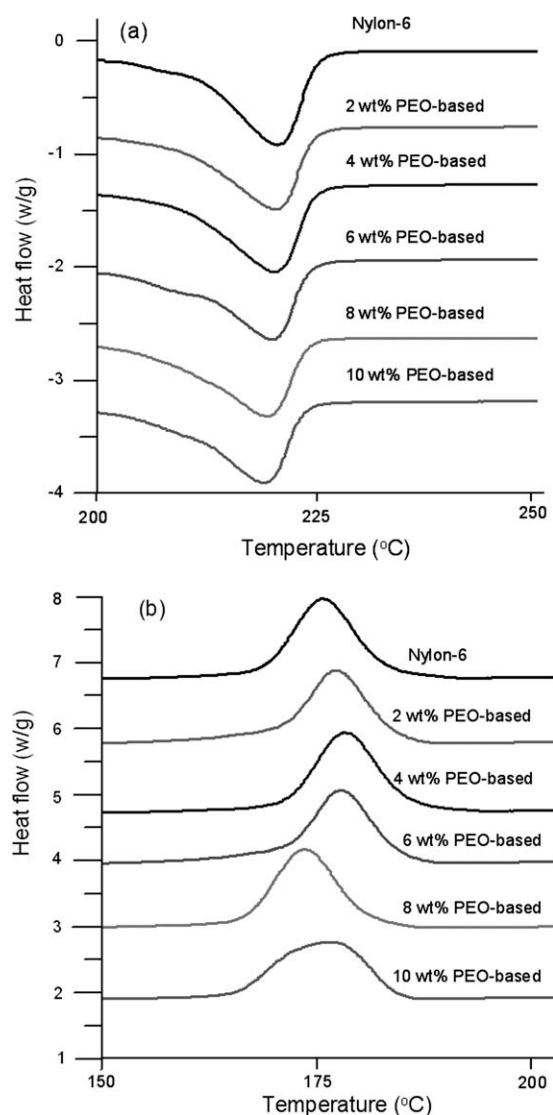
Figure 5 DSC scan curve of the prepared nylon-6/PEO copolymers. (a) DSC curve for detecting the melting temperature with various PEO content. (b) DSC cooling scan curve for determining the cold crystallization with various PEO.

Dynamic mechanical analysis

The T_g, which is associated with the relaxation of the main backbone chains in the amorphous phase was not readily determinable from the DSC results. Accordingly, this information was obtained from the tan δ curve. Figure 6 plots the curves of tan δ as a function of PEO for the copolymers. The samples exhibited similarly decreasing T_g with increasing PEO content due to the increase of the mobility in the polymer chain. The tan δ curve of the neat nylon-6 exhibits a transition at 62.3°C, which is an effect of the motion of large chain segments. The reduction in the T_g is attributed to the flexibility of the PEO segments. As PEO (soft segments) content increases, T_g declines, probably because of the plasticizing effect of the soft segments, which increases the mobility of the molecular chain in the
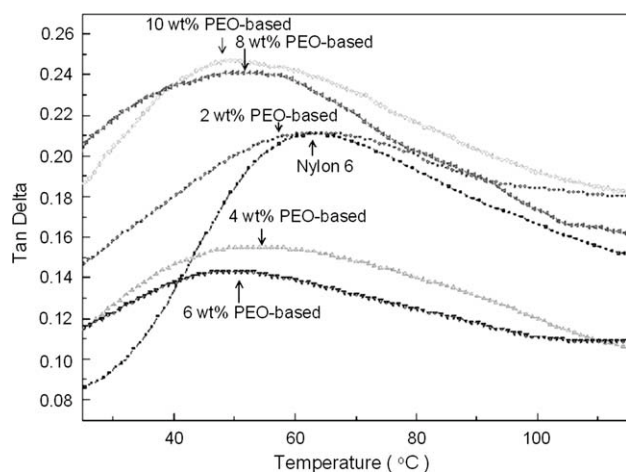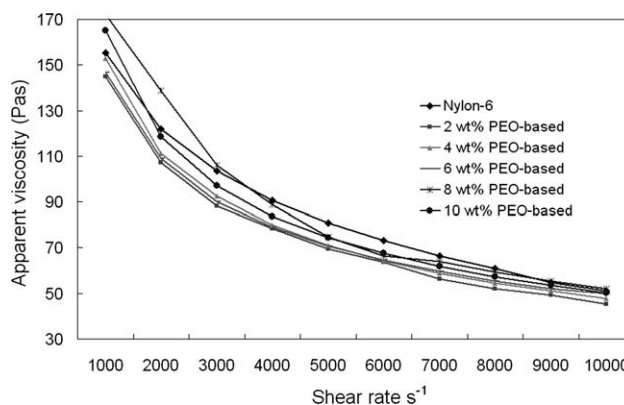
Figure 6 DMA curves of nylon-6 and copolymers with various PEO content.

Figure 7 Apparent viscosity versus non-Newtonian shear rate at various PEO content at 270°C.

copolymers. Meanwhile, PEO can penetrate into the sheets formed by the hydrogen bonds of the amide groups. This behavior is believed to be related to the breakage of hydrogen bonds between polymer chains, which induces long-range segmental chain movement in the amorphous area. The effect is pronounced up to 6 wt % of PEO, at which T_g is reduced by $\sim 10°C$ for T_g. The results for DSC and DMA could be explained that the relaxation of nylon-6 chains is influence by soft segments of PEO.

Table IV summarizes the thermal properties of the nylon-6/PEO copolymers. Interestingly, incorporating of less 10 wt % PEO into nylon-6 caused an insignificant change in T_m, T_c, but a significant decrease in the T_g value.

Measurement of capillary flow viscosity

Like that of linear polymers, the melt viscosity of the copolymers decreased as their shear rate increases. The rheology of copolymers as well as nylon-6 homopolymer exhibits shear-thinning. Figure 7 plots the apparent viscosities for various compositions at 270°C. With a low-shear rate, the viscosity is deter-

mined by molecular weight and chemical structure, whereas at high shear rate, the viscosity reflects the amount of residual entanglements during oriented chains. In the experiments herein, most of the copolymers exhibited a lower viscosity than nylon-6 at a lower shear rate (10^3 s^{-1}) because the PEO structures not only formed flexible bonds, but also decreased the amount of hydrogen bonding effect of the nylon-6 copolymers. The 2 wt % PEO copolymer had the lowest viscosity at a higher shear rate (10^4 s^{-1}), indicating its minimum molecular weight. This result was in an agreement with the amino end groups analysis from Table II. The melt viscosity varied insignificant with PEO content at a shear rate of 10^4 s^{-1}, suggesting that copolymers can be easily postprocessed like neat nylon-6.

Moisture absorption

Figure 8 reveals that the absorption of water increased with the amount of PEO in the nylon-6 matrix. PEO exhibits an important hydrophilic property, significantly raising the MR of the prepared copolymers. Introducing 10 wt % PEO into nylon-6 caused its MR value to triple after 48-h exposure at 25°C and a relative humidity, (RH), of 65%. Notably,

TABLE IV
**Thermal Properties of Nylon-6/PEO Copolymers**

wt % PEO	The melting temperature (°C)	$\star^1$ ΔH_m (J/g)	$\star^2$ Percentage crysatllinity (%)	The crystalline temperature (°C)	$\star^3$ ΔH_c (J/g)	The glass temperature (°C)
0	221.2	57.8	30.7	175.7	56.5	62.3
2	220.6	55.3	29.4	177.3	53.4	60.4
4	220.7	51.2	27.2	178.4	48.6	55.7
6	220.2	51.4	27.3	177.6	49	51.8
8	219.4	50.7	27.0	174.7	49.6	52.3
10	219.4	49	26.1	177.6	48.4	49.6

$\star^1$ ΔH_m (Enthalpy of fusion).
$\star^2$ Percentage crysatllinity (%) = ΔH_m(J/g)/188 (J/g). The enthalpy of fusion for nylon-6 crystalline fraction is 188 J/g [1].
$\star^3$ ΔH_c (Enthalpy of freeze).
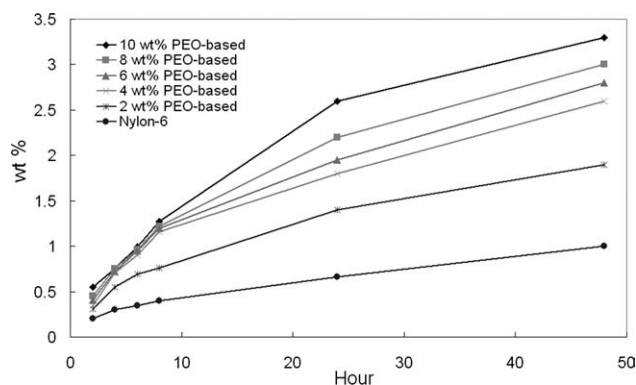
Figure 8 Moisture regain of nylon-6 and copolymers with various PEO content versus different exposure time.

the MR value of the nylon-6 chips reported herein was 0.9%, which was less than that 4.5% for typical nylon-6 fibers. That the fiber form but not the chip form has a large surface area is the main reason cause of the discrepancy. The fiber made from nylon-6/PEO copolymers is therefore believed to have a super moisture regain property, estimated to be
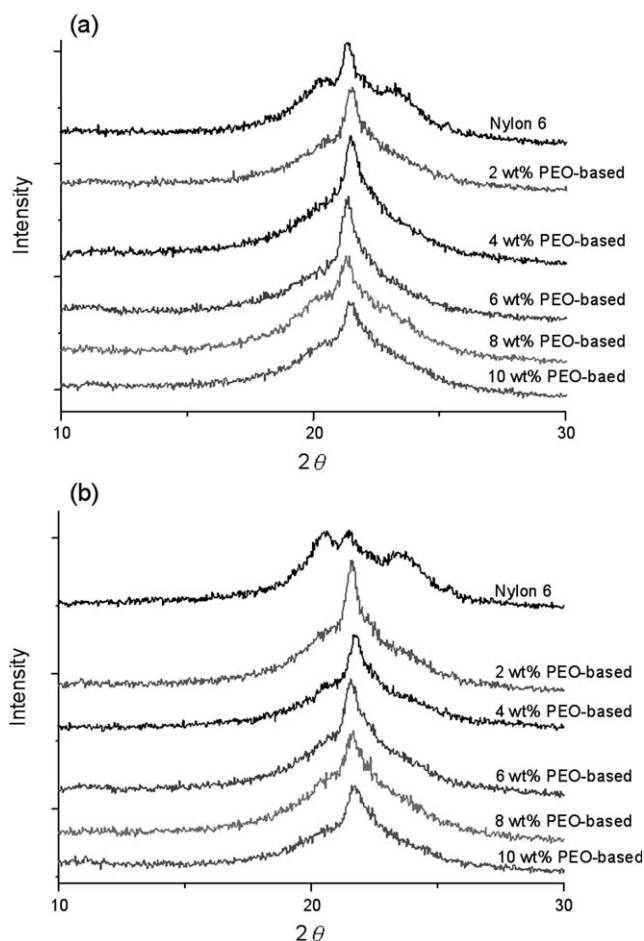
Figure 9 WAXS patterns of nylon-6 and copolymers with various PEO content. (a) Specimens before heat treatment. (b) Specimens after heat treatment.
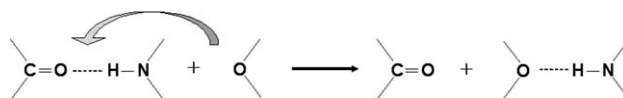
Scheme 2 Mechanism of breaking H-bond by PEO.

over 7 wt %, approaching the MR level of the cotton fiber, 8.5 wt %.[33] This characteristic has opened a new area in the "cool fiber" application, which is investigated currently and will be published in the future.

Wide-angle X-ray diffraction

WAXD experiments were carried on neat nylon-6 and its copolymers to determine their crystal structures. Three dominant diffraction peaks were obtained from neat nylon-6 [Fig. 9(a)]. Both appear at $2\theta = 20.5°$ and $2\theta = 23.5°$ are termed as the α crystalline phase. The other diffraction peak appear at $2\theta = 21.5°$ is termed the γ crystalline phase.[1] Unexpected diffraction peaks from PEO/nylon-6 are thus obtained in the experiments. The dominant crystalline structure was dramatically converted from α form to γ form when PEO was incorporated into the copolymers. These results suggest that the addition of PEO to nylon-6 changed the original crystal structure. PEO disfavored the α form and favored the γ form of the crystal. The α crystalline form of nylon-6 is reportedly associated with hydrogen bonds between adjacent antiparallel chains.[1] Therefore, the α form is converted into the γ form by breaking H-bonds between adjacent sheets of nylon-6. The molecular chains in nylon-6 are linked together by hydrogen bonds between C=O and N—H groups that contribute to the intermolecular force. Once PEO enters the backbone of nylon-6, the interactions between N—H and the ether groups (C—O—C) will alter the intermolecular structure. Yiping Qiu et al. demonstrated the moisture content significant affects the modifying effects of plasma treatment at atmospheric pressure. The original H-bonds are broken as water replaces the N—H groups.[34] A. Etxeberria proposed that the number of hydrogen bonds between the carbonyl and N—H groups declined as poly (ether amide) (PEA) content in nylon-6/PEA composition.[31]

Evidently, that the original hydrogen bonds were broken as a consequence of the PEO bonding with N—H group. The intermolecular hydrogen groups transformed from the pair of C=O, N—H to the pair of C—O—C, N—H is illustrated in Scheme 2. The addition of PEO disturbed the formation of the intersheet hydrogen bonds in the crystalline structure.
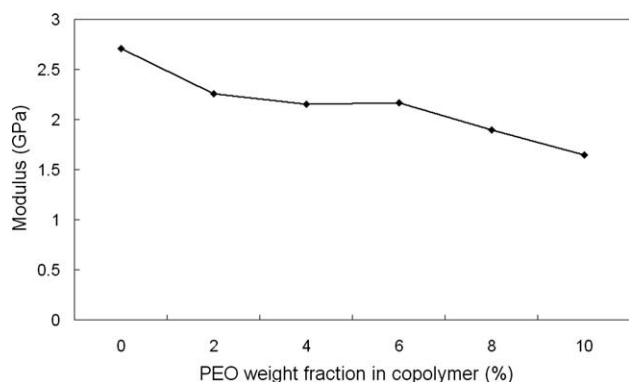
To verify exactly the interaction between amide and ether groups, all specimens underwent heat treatment. For nylon-6 crystals, the proportion of α
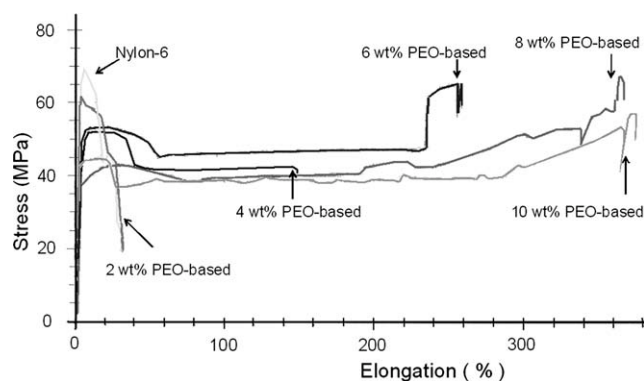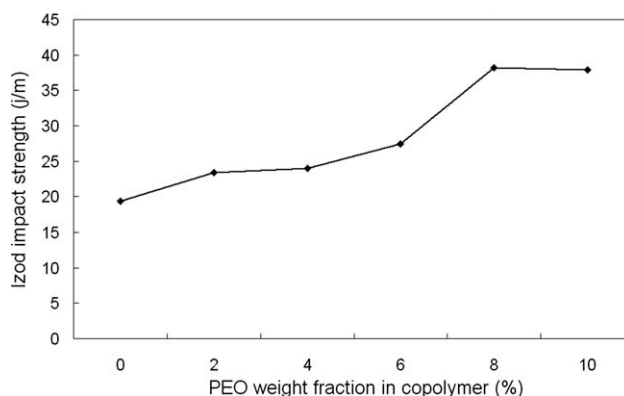
Figure 10 Tensile properties of nylon-6 and copolymers with various PEO content at room temperature.

Figure 12 Izod impact strength of nylon-6 and copolymers with various PEO content at room temperature.

forms increased with temperature and time of crystallization, suggesting that if the ether group does not any interact with the amide groups, then the crystal structure of copolymers will be converted from the γ form to the α form after heat treatment. On the contrary, if PEO were to interact with N—H, then the original hydrogen bond that is formed by the pair of C=O, N—H would be destroyed and new associations between N—H and C—O—C would be established. Thus, the γ from is still dominates the crystallinity. On the basis of this principle, the sheets were placed in a dryer, and maintained at 165°C under vacuum conditions. The annealing process lasted for 3 h, before WAXD experiments were performed. Figure 9(b) shows the results. The patterns revealed insignificant deviation between before and post heat treatment. However, the α form of neat nylon-6 continued to dominate the crystal structure ($2\theta = 20.5°$ and $2\theta = 23.5°$) and diffraction peaks of neat nylon-6 were stronger than before heat treatment. On the contrary, no transformations from the γ to the α form of the nylon-6/PEO copolymers was observed upon heat treatment. Comparing the diffraction peaks obtained between before and heat treatment further proved that the original hydrogen bond form the pair of C=O, N—H was replaced by

the pair of C—O—C, N—H. Consequently, no α crystal form of the copolymers was obtained in spite of annealing. The results concerning the crystal structure perhaps indicate that the formation of γ crystal is responsible for the slight downward shift in T_m.

Mechanical properties (tensile strength, elongation, modulus, Izod impact strength, heat distortion temperature)

The mechanical properties were measured, and Figure 10 presents the stress–strain profiles. Neat nylon-6 had a tensile stress of about 69 MPa and the elongation at breakage of approximately 36%. Adding PEO to nylon-6 significantly affected the observed mechanical properties. Clearly, the incorporation of PEO into the nylon-6 matrix dramatically increased the tensile elongation. The copolymers with 6 wt % and 8 wt % PEO had seven to ten times greater elongation at breakage (257%, 364%), revealing that incorporating PEO into nylon-6 considerably affected its stiffness and toughness probably because PEO forms soft parts in the nylon-6 matrix and reduces the crystallinity, also improving elongation. However, the tensile strength of copolymer at breakage decreased with the amount of added PEO. At 10

Figure 11 Modulus of nylon-6 and copolymers with various PEO content at room temperature.
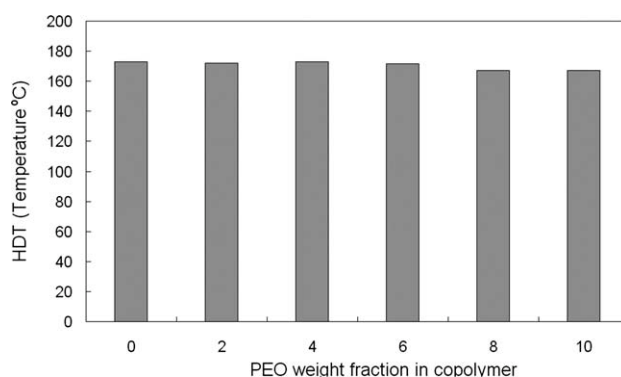
Figure 13 HDT of nylon-6 and copolymers with various PEO content.

Mechanical Properties of Nylon-6/PEO Copolymers

wt % PEO	Tensile strength (MPa)	Elongation at break (%)	Modulus (GPa)	Izod impact strength (J/m)	HDT (°C)
0	69	36	2.71	19.34	172.9
2	62	37	2.23	23.34	171.9
4	54	148	2.15	23.94	172.8
6	65	259	2.17	27.40	171.6
8	67	367	1.90	38.21	167.4
10	57	373	1.65	37.90	167.1

wt % PEO copolymer, the tensile strength is 57 MPa. The value is approximately 12 MPa lower, than those of neat nylon-6. The tensile strength is known to be sensitive to the properties of the interface between neighboring segments; the intermolecular force between PEO and nylon-6 is weaker than that within nylon-6. The worsening of the tensile properties is partially caused by a drop in crystallinity of copolymers or a change in the dominant crystalline phase from α to γ, as discussed in the previous section. Thus, the copolymers exhibited excellent ductility, but decreased tenacity. Clearly, the incorporation of PEO into the nylon-6 matrix reduces tensile strength and Young's modulus, making the copolymers softer and more flexible than the neat nylon-6. Therefore, the PEO segments are thought to have negative effects on both the tenacity and modulus of the copolymers. As shown in Figure 11, neat nylon-6 has a modulus of 2.7 GPa, while copolymer with 10 wt % PEO loading has a reduced modulus of 1.6 GPa, implying that the PEO makes the copolymers more ductile but less stiff. Figure 12 plots the notched Izod impact strength of the copolymers as a function of PEO content. The Izod impact strength of the copolymers is better than that of neat nylon-6. Related results reveal that adding 8 wt % PEO to copolymers increased Izod impact strength to 40 J/m—around double that of neat nylon-6. The reason for this remarkable enhancement is believed to be associated with the interactions between the ether portion of PEO and the amide group of nylon-6, which reduces the rigidity of the structure of the copolymers. Another explanation involves the absorption of energy by either vibration or rotation of ether groups. The PEO soft segments act as a plasticizer, increasing the mobility of the molecular chain in the copolymers.

To obtain further mechanical information, HDT was investigated. Figure 13 demonstrates that the HDT of copolymers decreased as PEO content increased. Neat nylon-6 had an HDT of approximately172.9°C. The stiffness was maintained beyond T_g because nylon-6 and its copolymers are semicrystalline. HDT changes insignificantly until the PEO content reached 6 wt %, increasing by only 1.3°C from that of neat nylon-6. However, HDT decreased

apparently as the PEO content increases over 8 wt %. The HDT of copolymers with 8 wt % and 10 wt % were around 5.5 and 5.8°C lower, respectively, than that of neat nylon-6. The decrease in the HDT with increasing PEO content is assumed to be caused by the decrease in the crystallinity or a change in the less stable γ phase. Another probably cause is the plasticizing effect of the flexibility of PEO.

Table V summarizes the mechanical properties of the nylon-6/PEO copolymers. Some of results of the mechanical tests are in good agreement with the behavior elucidated by DMA.

CONCLUSIONS

We have been successfully synthesized nylon-6/PEO copolymer system based on feed ratio of PEO (0 ~ 10 wt %) through condensation polymerization with moderate molecular weight as confirmed by amino end group analysis. FT-IR validates the structure as nylon-6 and ^{1}H-NMR spectra characterized the PEO content of each copolymer system. With respect to thermal properties determined by DSC, both T_m and T_c slightly decreased as the PEO content in copolymers increased. The prepared copolymers had slight lower tenacity, modulus, and HDT than neat nylon-6, but significantly greater elongation and Izod impact strength. When the PEO content in the copolymer was less than 10 wt %, the thermal behaviors were almost identical to those of neat nylon-6, but the mechanical performance differed markedly. Introducing 8 wt % PEO into nylon-6 increased its impact strength and elongation by factors of ~ 2 and 10, respectively. The DMA-determined agrees closely with that determined by mechanical testing. The plasticizing effect of the soft segments of PEO increases the mobility of the molecular chain in the copolymers. Consequently, the T_g of copolymers declines as the PEO content increases. Rheological investigation indicated that neat nylon-6 and its copolymer behaved similarly at high shear rates. The moisture regain of the prepared copolymers improved in proportion to the PEO content. Adding a little PEO to the copolymer altered its crystallinity from α form to γ form, mainly by breaking up parts

of the original H-bonds by the incorporation of ether groups.

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