

Synthesis and Hydrophilicities of Poly(ethylene 2,6-naphthalate)/Poly(ethylene glycol) Copolymers

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(Received October 1, 2003; Revised December 9, 2003; Accepted December 16, 2003)

Abstract: Poly(ethylene 2,6-naphthalate) (PEN)/Poly(ethylene glycol) (PEG) copolymers were synthesized by two step reaction during the melt copolymerization process. The first step was the esterification reaction of dimethyl-2,6-naphthalenedicarboxylate (2,6-NDC) and ethylene glycol (EG). The second step was the condensation polymerization of bishydroxyethylnaphthalate (BHEN) and PEG. The copolymers contained 10 mol% of PEG units with different molecular weights. Structures and thermal properties of the copolymers were studied by using $^1\text{H-NMR}$, DSC, TGA, etc. Especially, while the intrinsic viscosities of PEN/PEG copolymers increased with increasing molecular weights of PEG, but the glass transition temperature, the cold crystallization temperature, and the weight loss temperature of the copolymers decreased with increasing molecular weights of PEG. Consequently, the hydrophilicities by means of contact angle measurement and moisture content of the copolymer films were found to be significantly improved with increasing molecular weights of PEG.

Keywords: Poly(ethylene 2,6-naphthalate), Poly(ethylene glycol), Melt copolymerization, Hydrophilicities, Contact angle

Introduction

Poly(ethylene 2,6-naphthalate) (PEN) is a useful engineering thermoplastic material with a good thermal stability, excellent mechanical and chemical properties [1-3]. It is also an aromatic polyester whose chemical structure is similar to that of poly(ethylene terephthalate) (PET) [4]. However, PEN has thermal, mechanical, electrical and barrier properties as well as its heat, chemical, hydrolytic and radiation resistance which are generally superior to those of PET [5,6]. The most important feature of PEN compared to PET is the increased stiffness of its macro-molecular chain due to the presence of a naphthalene ring instead of a benzene ring [7]. In other words, the difference can be attributed to the difference in the deformability between the naphthalene and phenyl rings, because in contrast to the conformation of PET, all atoms of the PEN chain including O-CH₂ are coplanar [8].

In recent years, there has been a great deal of interest in the PEN for the applications of technical textiles, films, and rubber goods, etc. Nevertheless, not only the production cost of PEN until now has been much higher than that of PET, but also PEN has been some shortcomings such as poor antistatic property, low hygroscopicity, poor dyeability, and difficult plastic processing. These properties may limit its use. In this regard, many studies have been carried out to improve the properties of PEN. However, most of previous studies were devoted to explore the morphology, thermal behaviors, mechanical property and crystallization behaviors of PEN [9-17]. No studies have been published on the hydrophilicity and surface modification of PEN in the literature.

On the other hand, poly(ethylene glycol) (PEG) is a hydrophilic polymer, it has various properties with its molecular

weights [15,16]. PEG is also nontoxic polymer with outstanding physicochemical and biological properties. It has very good antistatic property and biocompatibility, solubility in water and many organic solvents, lack of immunogenicity, high mobility and large exclusion volume in water [18]. Moreover, when PEG is coupled to other molecules, many of these properties may be transferred to the conjugated product. It is well known that PEG is still being employed to improve the hydrophilicity of synthetic polymer. Accordingly, it is expected that if the diol unit of hydrophilic PEG polymer incorporates to the backbone of hydrophobic PEN polymer chain, the hydrophilicities of PEN will be greatly improved.

In this study, PEN/PEG copolymers with different molecular weights of PEG were synthesized by melt copolymerization process. The effects of PEG molecular weights on the thermal and surface properties of PEN/PEG copolymers were investigated.

Experimental

Materials

Dimethyl-2,6-naphthalenedicarboxylate (2,6-NDC) were supplied by Hyosung Co. Ethylene glycol (EG) and five PEGs of number average molecular weights (M_n) of 400, 900, 2000, 3400, and 4600 were purchased from Aldrich Chemical Co.

Zinc acetate, antimony trioxide, and trimethyl phosphate (Aldrich) were used as catalysts for copolymerization. Analytical grade deuterated chloroform and trifluoroacetic acid (Aldrich) were used as $^1\text{H-NMR}$ solvents and other reagents of extraordinarily pure grade were used as received.

Synthesis of PEN/ PEG Copolymer

The synthesis of copolymers was carried out in an autoclave equipped with a ribbon-type stirrer, an electronic heater, and

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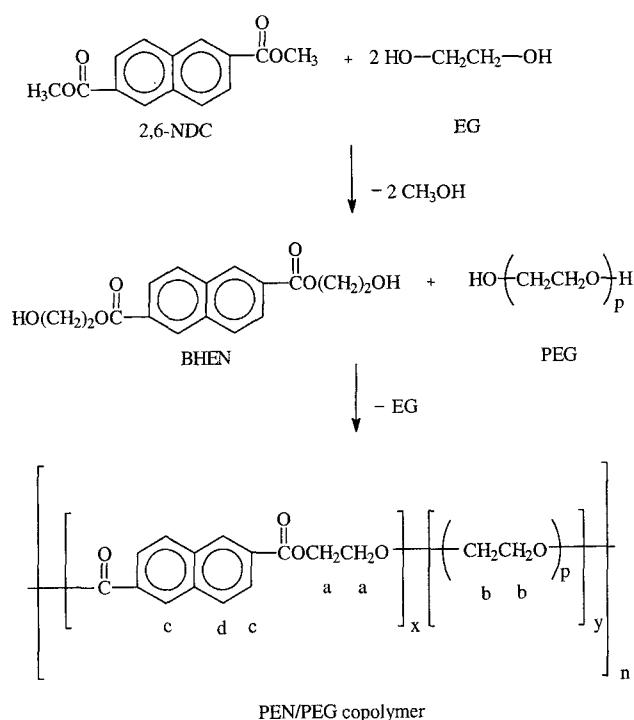


Figure 1. Synthesis scheme of PEN/PEG copolymer.

a temperature controller. PEN/PEG copolymers with different molecular weights of PEG were synthesized by two step reaction during the melt copolymerization process according to the procedure as shown in Figure 1. The first step was the esterification reaction of 2,6-NDC with EG (molar ratio of 2,6-NDC/EG = 1:2) using zinc acetate as a catalyst. The second step was the condensation polymerization of bishydroxyethyl-naphthalate (BHEN) with PEG using antimony trioxide as a catalyst. The esterification reaction was performed at 230 °C under nitrogen atmosphere, and the condensation polymerization was performed at 285 °C for 3 h *in vacuo* of 0.5 Torr. PEN/PEG copolymer films were prepared by melt casting. The casting method carried out at a temperature of 280 °C and then the films were quenched into ice water. The thickness of film was 0.2 mm.

Characterization

Intrinsic viscosity $[\eta]$ measurements of the PEN/PEG copolymers were performed using an automatic IV measuring system (AVS 360, Germany) equipped with an Ubbelohde viscometer at 30 °C in a solvent of *o*-chlorophenol. $^1\text{H-NMR}$ spectra were obtained with a Varian Gemini NMR spectrometer at 200 MHz. The samples were dissolved in a mixture solution of deuterated chloroform and trifluoroacetic acid (70/30, w/w) using tetramethylsilane as an internal reference. Thermal behaviors of the copolymers were observed by differential scanning calorimetry and thermogravimetry with DSC (TA 2100) and TGA (TA Q50), respectively. DSC and

TGA experiments were conducted from -50 to 300 °C and from 50 to 700 °C, respectively, at a heating rate of 10 °C/min under nitrogen atmosphere. The contact angle of PEN/PEG copolymer films was measured by using a contact angle & surface tension analyzer (SEO, Phoenix 300). The contact angle measurement was performed by the sessile drop method. The sessile drop experiment consists of placing a known volume of a water drop (10 μl of distilled water) on the copolymer film surface. The moisture content of the copolymer films was measured under standard atmosphere for conditioning and testing textiles, it was calculated using the following equation:

$$\text{Moisture content (\%)} = B - A / B \times 100 \quad (1)$$

Where *A* is the weight of the dried sample (105 °C, 2 h) and *B* is the weight of the conditioned sample (65 % RH, 20 °C, 24 h).

Results and Discussion

$^1\text{H-NMR}$ Analysis

As shown in Figure 2, the peak due to ethylene unit (a) for pure PEN appeared at 4.92 ppm. Also, the peaks due to the naphthalene ring unit for pure PEN appeared at 8.13 (c) and 8.72 (d) ppm. The peak due to ethylene unit (b) for pure PEG appeared at 3.82 ppm. In case of PEN/PEG copolymer, as shown in Figure 2, it was confirmed that not only (a) and (b) peaks due to ethylene unit for PEN and PEG, but also (c) and (d) peaks due to naphthalene ring unit for PEN are all appeared in the copolymers. The compositions of PEN/PEG copolymers were determined from $^1\text{H-NMR}$ spectra as shown in Figure 2. Two main peaks were used for the

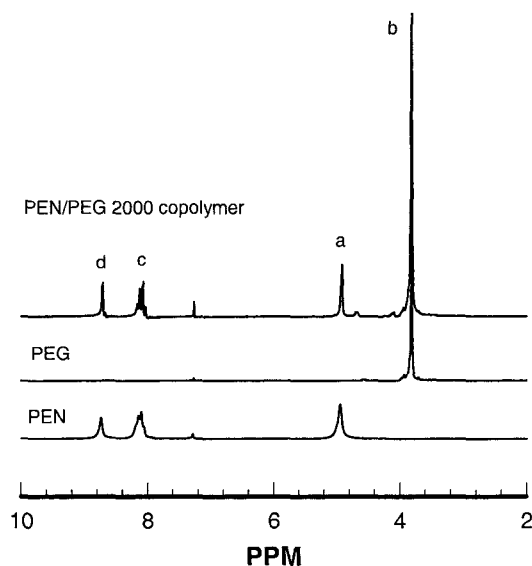


Figure 2. $^1\text{H-NMR}$ spectra of PEN, PEG, and PEN/PEG 2000 copolymer.

Table 1. Comparison of feed composition and copolymer composition, and intrinsic viscosities $[\eta]$ of PEN/PEG copolymers

Samples	PEG (mol %)		PEN (mol %)		$[\eta]$ (dl/g)
	Feed composition	Copolymer composition	Feed composition	Copolymer composition	
PEN			100	100	0.66
PEN/PEG 400	10	7.0	90	93.0	0.64
PEN/PEG 900	10	11.8	90	88.2	0.78
PEN/PEG 2000	10	11.2	90	88.8	0.82
PEN/PEG 3400	10	10.2	90	89.8	0.86
PEN/PEG 4600	10	11.0	90	89.0	0.87

determination: one for the ethylene unit of PEN (a: 4.92 ppm) and the other for the ethylene unit of PEG (b: 3.82 ppm), respectively. Thus, molar compositions were calculated as the equations (2) and (3):

$$\text{PEN (mol \%)} = [a/(a + b)] \times 100 \quad (2)$$

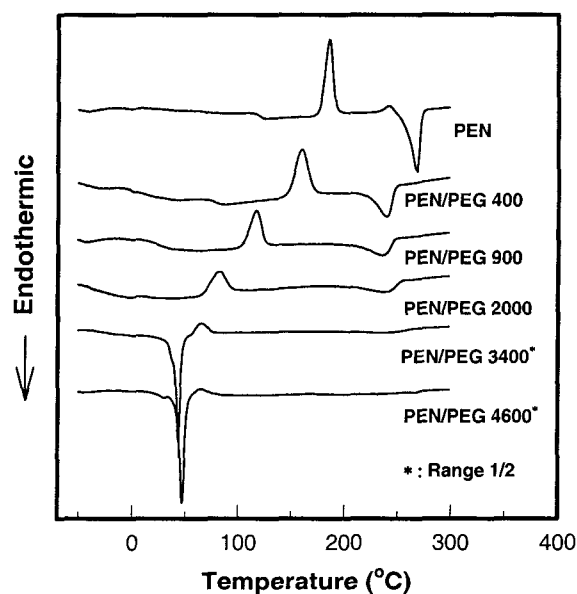
$$\text{PEG (mol \%)} = [b/(a + b)] \times 100 \quad (3)$$

The feed composition and copolymer composition calculated from these equations are listed in Table 1. It can be seen that the molar ratio of copolymer composition is about the same as that of the feed composition for PEN/PEG copolymers which the molecular weight of PEG are 900-4600. However, a discrepancy between copolymer composition and feed composition was observed for PEN/PEG 400 copolymer. The difference could be explained that the evolution of low molecular weight PEG may occur more readily than that of high molecular weight PEG due to its higher volatility during the melt copolymerization process under high vacuum condition [6]. On the other hand, the intrinsic viscosity $[\eta]$ of PEN/PEG copolymers was simultaneously presented in Table 1. The $[\eta]$ of the polymers with increasing molecular weights of PEG were almost increased except the PEN/PEG 400 copolymer. It is assumed that the $[\eta]$ of copolymer is enhanced by the incorporation of higher molecular weight PEG moiety into the PEN molecular chain.

Thermal Behaviors

Figure 3 shows DSC curves of PEN/PEG copolymers with different molecular weights of PEG. The glass transition temperature (T_g) and the cold crystallization temperature (T_{cc}) of pure PEN are 119 and 184 °C, respectively. In the DSC curve of the copolymers, T_g was observed in PEN/PEG 400 and PEN/PEG 900 copolymers and decreased with increasing molecular weights of PEG. However, T_g of PEN/PEG 2000, PEN/PEG 3400, and PEN/PEG 4600 copolymers did not observed. Also, T_{cc} of the PEN/PEG copolymers were always observed and decreased with increasing molecular weights of PEG. It is assumed that the decreases of T_g and T_{cc} are due to the increased flexibility and mobility of copolymer chains by introduction of long flexible PEG molecular chain.

Table 2 shows the thermal transition temperatures of PEN/

**Figure 3.** DSC curves of PEN/PEG copolymers with different molecular weights of PEG.**Table 2.** Thermal transition temperatures of PEN/PEG copolymers measured by DSC

Samples	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_f (J/g)
PEN	119.4	184.6	268.1	34.0
PEN/PEG 400	76.9	159.0	239.8	20.9
PEN/PEG 900	22.3	117.0	236.8	21.6
PEN/PEG 2000	-	82.5	241.4	20.6
PEN/PEG 3400	-	67.4	42.8	92.5
PEN/PEG 4600	-	64.4	49.0	93.0

PEG copolymers measured by DSC. As shown in Table 2, the melting temperature (T_m) and the heat of fusion (ΔH_f) of pure PEN are 268 °C and 34 J/g, respectively. In case of PEN/PEG 400-PEN/PEG 2000 copolymers, T_m and ΔH_f of the copolymers were decreased compared with pure PEN. It is assumed that the decreases of T_m and ΔH_f of the copolymers are due to the increased chain disorder with the addition of PEG. Especially, T_m for PEN/PEG 3400 and PEN/PEG 4600 copolymers are 42 and 47 °C, respectively. This is due to

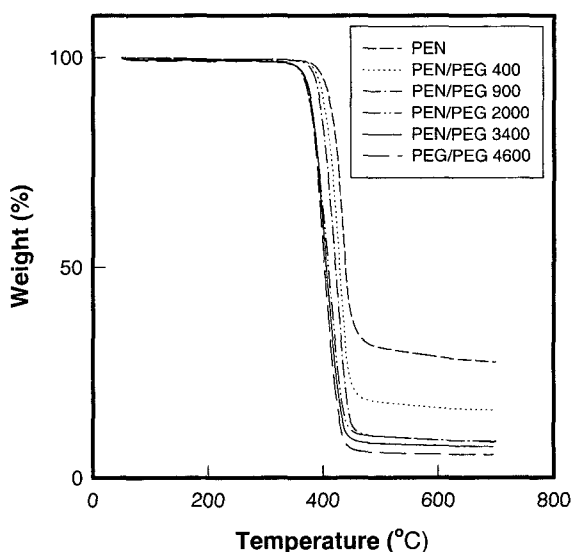


Figure 4. TGA curves of PEN/PEG copolymers with different molecular weights of PEG.

Table 3. Temperatures of 5 % and 50 % weight loss of PEN/PEG copolymers

Samples	Temp. of 5 % weight loss (°C)	Temp. of 50 % weight loss (°C)
PEN	400	439
PEN/PEG 400	391	429
PEN/PEG 900	386	422
PEN/PEG 2000	366	409
PEN/PEG 3400	369	406
PEN/PEG 4600	368	403

only T_m of PEG without T_m of PEN. Raquez *et al.* [19] has been reported that T_m of PEG molecular weight of 4000 is 60 °C. It is assumed that the T_m of PEN/PEG 3400 and PEN/PEG 4600 copolymer became lower than that of PEG molecular weight of 4000 is because the PEN component in copolymer has an influence on the crystallization of PEG. Also, no T_m due to PEN is seen in the copolymer, which may be due to incomplete formation of PEN domain.

Figure 4 shows TGA curves of PEN/PEG copolymers. It is shown that the thermal decomposition temperatures of the copolymers decreased with increasing molecular weights of PEG. Simultaneously, Table 3 shows temperatures of 5 % and 50 % weight loss of the copolymers with different molecular weights of PEG. 5 % and 50 % weight loss temperatures of pure PEN are 400 and 439 °C, respectively. In case of PEN/PEG 400-PEN/PEG 4600 copolymers, 5 % and 50 % weight loss temperatures of the copolymers were decreased compared with pure PEN. Especially 5 % and 50 % weight loss temperatures of the copolymers were markedly decreased above 2000 of PEG molecular weights. It can be explained that the

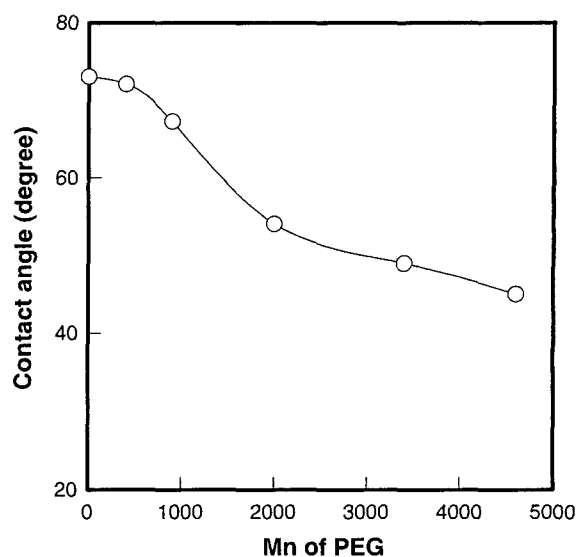


Figure 5. Contact angles of PEN/PEG copolymer films using water with different molecular weights of PEG.

thermal stability of the copolymers is decreased due to the low thermal stability of PEG.

Surface Properties

The hydrophilicities of PEN/PEG copolymer films were observed by measurements of contact angle and moisture content. Figure 5 shows the changes in the contact angles of PEN/PEG copolymer films using water with different molecular weights of PEG. As shown in Figure 5, the contact angle on the surface of pure PEN film is 73 °, and the contact angles on the surface of PEN/PEG 400 and PEN/PEG 900 copolymer films are 72 and 67 °, respectively. The pure PEN was presented the highest degree indicating that the surface is hydrophobic and PEN/PEG 900 copolymer film was decreased by the contact angle of approximately 6 ° compared with pure PEN film. The contact angles on the surface of PEN/PEG 2000-PEN/PEG 4600 copolymer films are 54-45 ° and markedly decreased about 19-28 ° compared with PEN of 73 °. It was confirmed that the contact angles on the surfaces of the copolymer films were greatly decreased with increasing molecular weights of PEG.

Figure 6 shows the changes in the moisture contents of PEN/PEG copolymer films with different molecular weights of PEG. The moisture content of pure PEN is about 0.2 %. The moisture contents of PEN/PEG 400 and PEN/PEG 900 copolymer films are about 0.7-1.2 %. Also, the moisture contents of PEN/PEG 2000-PEN/PEG 4600 copolymer films are about 2.7-5.9 %. It was confirmed that the moisture contents of the copolymer films were markedly increased with increasing molecular weights of PEG. Accordingly, from the results of Figures 5 and 6, it can be concluded that the hydrophilicities by means of the evaluation of contact angle measurement and moisture content of the copolymer films

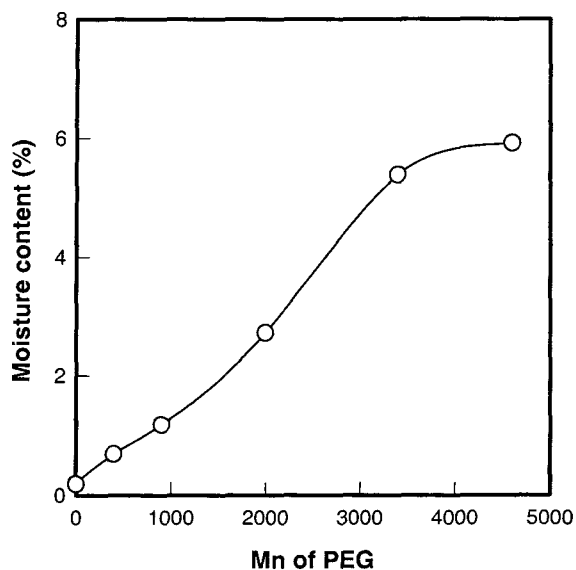


Figure 6. Moisture contents of PEN/PEG copolymer films with different molecular weights of PEG.

were significantly improved with increasing molecular weights of PEG.

Conclusions

PEN/PEG copolymers were synthesized by melt copolymerization process of 2,6-NDC, EG, and PEG. The copolymers contained 10 mol% of PEG units with different molecular weights. The effects of PEG molecular weights on the thermal and surface properties of PEN/PEG copolymers were investigated.

It was confirmed that the molar ratio of copolymer composition is about the same as that of feed composition for PEN/PEG copolymers which the number average molecular weights of PEG are 900-4600. According as the increasing molecular weights of PEG, the $[\eta]$ of PEN/PEG copolymers increased. However, T_m , T_g , T_{cc} and the temperatures of 5% and 50% weight loss of PEN/PEG copolymers decreased compared with those of PEN with increasing molecular weights of PEG. Consequently, the hydrophilicities by means of the evaluation of contact angle measurement and moisture content of the copolymer films were found to be significantly

improved with increasing molecular weights of PEG.

Acknowledgement

The present study was conducted by the research fund of Dankook University in 2002.

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