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

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ABSTRACT: Poly(butylene 2,6-naphthalate) (PBN)/poly-(ethylene glycol) (PEG) copolymers were synthesized by the two-step melt copolymerization process of dimethyl-2,6-naphthalenedicarboxylate (2,6-NDC) with 1,4-butanediol (BD) and PEG. The copolymers produced had different PEG molecular weights and contents. The structures, thermal properties, and hydrophilicities of these copolymers were studied by ^{1}H NMR, DSC, TGA, and by contact angle and moisture content measurements. In particular, the intrinsic viscosities of PBN/PEG copolymers increased with increasing PEG molecular weights, but the melting temperatures (T_m), the cold crystallization temperatures (T_{cc}), and the heat of fusion (ΔH_f) values of PBN/PEG copolymers decreased on increasing PEG contents or molecular weights. The thermal stabilities of the copolymers were unaffected by PEG content or molecular weight. Hydrophilicities as determined by contact angle and moisture content measurements were found to be significantly increased on increasing PEG contents and molecular weights. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2677–2683, 2006

Key words: poly(butylene 2,6-naphthalate); poly(ethylene glycol); hydrophilicity; melt copolymerization; contact angle

INTRODUCTION

Poly(butylene 2,6-naphthalate) (PBN) is derived from dimethyl-2,6-naphthalenedicarboxylate (2,6-NDC) and 1,4-butanediol (BD), and is a linear aromatic polyester, which is composed of repeated units of a flexible butylene group units and naphthalene rings that can induce strong interchain interactions.[1] PBN is also a thermoplastic polymer with a chemical structure similar to that of poly(butylene terephthalate) (PBT). However, PBN has thermal, mechanical, and insulating properties and chemical, hydrolytic, and radiation resistance properties that are generally superior to those of PBT.[2–4] The most important feature of PBN compared with that of PBT is the increased stiffness of its macromolecular chain due to the presence of a naphthalene ring instead of a benzene ring.[5]

Applications for PBN include biaxially oriented films, connectors, switches, coil bobbins, ignition coils, fuel sensors, fuel tanks, and hoses. However, the production costs of PBN are much higher than those of PBT, and PBN has other shortcomings such as its poor antistatic, hygroscopicity, dyeability, and plastic processing properties, which limit its usefulness. In recent years, PBN has been studied extensively in terms of its crystallization, crystal structure, melting, and melt-recrystallization properties.[6–10] Some interesting studies have also been undertaken on other naphthalate-based copolymers.[11–13] However, to the best of our knowledge, no studies have yet been conducted on the hydrophilic modifications of PBN.

Poly(ethylene glycol) (PEG) is a hydrophilic and nontoxic polymer with outstanding antistatic and biocompatible properties.[14–16] Moreover, it is known that when PEG is coupled to other molecules, many of its properties are transferred. Moreover, PEG is used to improve the hydrophilicities of synthetic polymers.[17] Thus, we considered that the hydrophilicity of PBN could be improved by introducing PEG, and that the copolymers produced would have hydrophilicity and thermal properties distanced from those of pure PBN.

In this study, the esterification and condensation polymerizations were used to synthesize PBN/PEG copolymers as a melt. In addition, we examined the effects of PEG content and molecular weight on the thermal properties and hydrophilicities of the copolymers produced.

EXPERIMENTAL

Materials

Dimethyl-2,6-naphthalenedicarboxylate (2,6-NDC) was purchased from Hyosung (Seoul, Korea), and BD and poly(ethylene glycol) (PEG) were purchased from Aldrich. The number average molecular

weights (M_n) of the PEGs used were 400, 900, 2000, and 3400 g/mol. Tetrabutyl orthotitanate (Aldrich) was used as a copolymerization catalyst. Analytical grades of deuterated chloroform and trifluoroacetic acid (Aldrich) were used as ^{1}H NMR solvents, all other reagents were of the purest grades commercially available and were used as received.

Synthesis of PBN/PEG copolymer

The syntheses of PBN homopolymer and PBN/PEG copolymers were carried out in an autoclave equipped with a ribbon-type stirrer, an electronic heater, and a temperature controller. Copolymers were prepared by either changing PEG molecular weight or PEG content in a two-step copolymerization process, according to the procedure shown in Figure 1. In the first step, oligomers were prepared with 2,6-NDC, BD, and PEG using tetrabutyl orthotitanate as a catalyst by esterification, and in the second step, these oligomers were condensed to form polymers by condensation polymerization. The esterification was performed for 3 h at 210°C in a nitrogen atmosphere, until the methanol was not produced any more. The condensation polymerization was performed at 260°C for 2 h *in vacuo* of 0.5 Torr.

PBN/PEG copolymer films were prepared by melt casting. Casting was carried out at 280°C, and cast films were quenched with iced water. Film thicknesses were 0.1 mm.

Characterization

Intrinsic viscosities [η] of PBN/PEG copolymers were determined at 30°C in *o*-chlorophenol, using an automatic IV measuring system (AVS 360, Germany) equipped with an Ubbelohde viscometer.

^{1}H NMR spectra were obtained using a Varian Gemini NMR spectrometer at 200 MHz. Samples were dissolved in a solution of deuterated chloroform and trifluoroacetic acid (70/30, w/w) using tetramethylsilane as an internal reference.

Copolymer thermal properties were examined using a differential scanning calorimeter (DSC, TA2010) under a nitrogen atmosphere. Samples were placed in a DSC pan and maintained at 290°C for 5 min to erase any previous thermal history. They were then immediately quenched in a liquid nitrogen and reheated at 20°C/min from 0 to 300°C.

Thermogravimetric analysis was carried out using a thermogravimetric analyzer (TGA, TA Q50), at a scanning rate of 20°C/min from 30 to 600°C in a nitrogen atmosphere.

PBN/PEG copolymer film contact angles were measured using a contact angle and surface tension analyzer (SEO, Phoenix 300). Contact angles were measured using the sessile drop method. Briefly, this in-

volves placing a distilled water drop of known volume (10 μL) on a copolymer film surface and measuring its contact angle.[18]

The amounts of water in the copolymer films were measured after conditioning in a standard atmosphere (65% RH, 20°C, 24 h), and the results are expressed as the percentages of moisture contents on the weights of dried films (105°C, 2 h).

RESULTS AND DISCUSSION

^{1}H NMR analysis

Figure 2 shows ^{1}H NMR spectra of PBN/PEG copolymer, pure PBN, and PEG (M_n 2000). The proton peaks due to butylene unit in pure PBN appeared at 2.16 ppm (a) and 4.62 ppm (b), respectively. And the proton peaks due to the naphthalene ring in pure PBN appeared at 8.13 ppm (e) and 8.72 ppm (d), respectively. The peak due to the ethylene unit (c) in pure PEG appeared at 3.82 ppm. In the case of PBN/PEG copolymer containing PEG of M_n 2000, peaks (a), (b), and (c), due to the butylene and ethylene units of PBN and PEG, were present, in addition to the naphthalenic peaks (d) and (e) of PBN. PBN/PEG compositions were determined from ^{1}H NMR spectra, as shown in Figure 2.

Three peaks were used to determine compositions, namely, the 3.82 ppm PEG ethylene unit peak (c) and the 2.16 ppm and 4.62 ppm PBN butylene unit peaks (a and b), respectively. Molar compositions were calculated using eqs. (1) and (2):

$$PBN \ (mol \ \%) \ = \ [f/(c + f)] \times 100 \quad (1)$$

$$PEG \ (mol \ \%) \ = \ [c/(c + f)] \times 100 \quad (2)$$

where $f = (a + b)/2$.

The feed compositions and copolymer compositions calculated using these equations are listed in Table I. The table shows that the copolymer compositions are as expected for the PEG and BD feed compositions. Moreover, our results show that copolymerization went to completion.

The intrinsic viscosities [η] of PBN/PEG copolymers produced are presented in Table I. Copolymer's [η] values increased with increasing PEG molecular weights and contents. We believe that copolymer [η] values were enhanced by incorporating higher molecular weight PEG into PBN.

Thermal behaviors

Figure 3 shows the DSC curves of quenched PBN/PEG copolymers containing PEGs with different molecular weights. In general, the molecules of most semicrystalline polymers can be maintained in a ran-
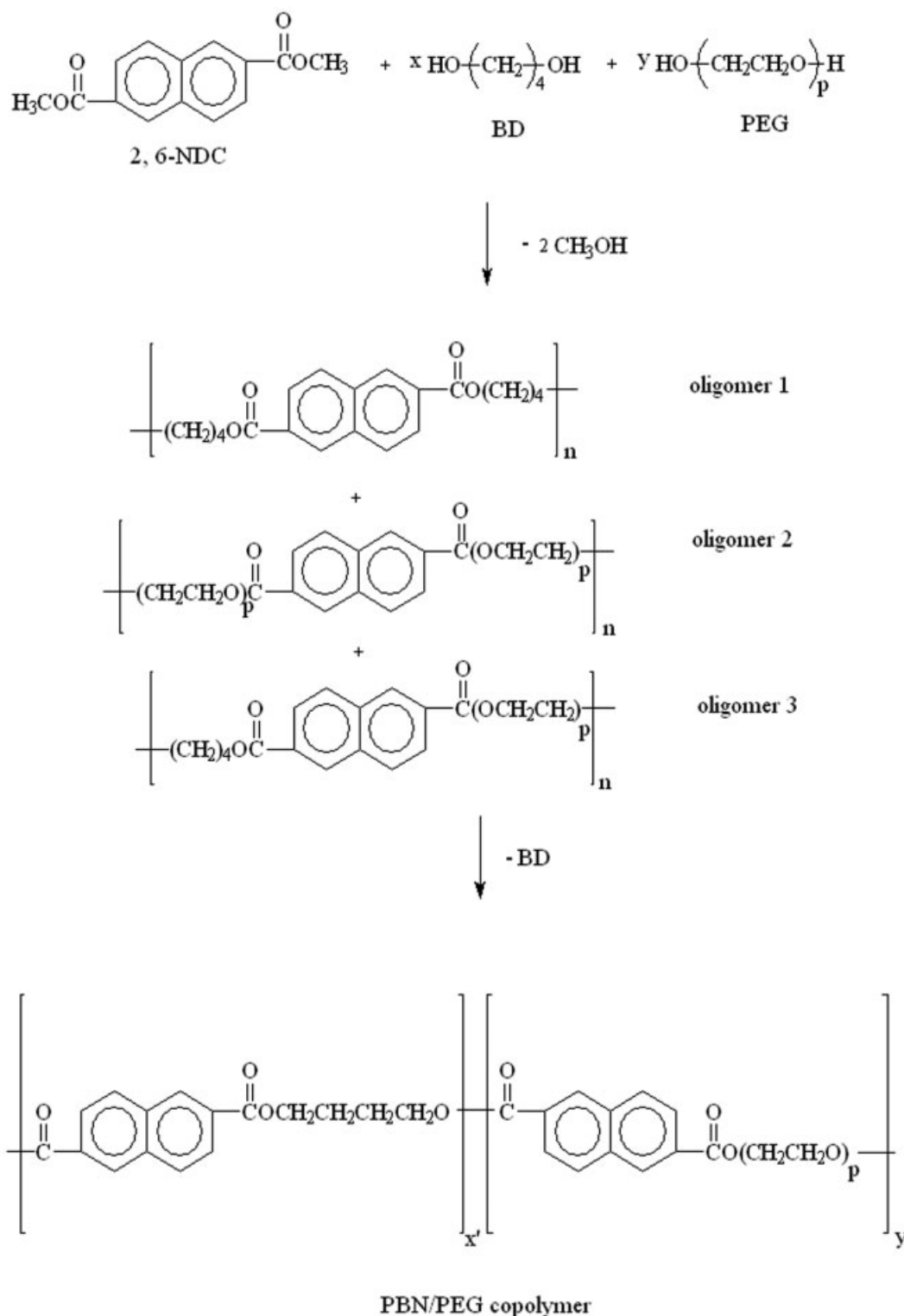
Figure 1 Synthesis scheme of PBN/PEG copolymer.

dom state by melt quenching, which enables glass transition temperatures (T_g) and exotherms resulting from cold crystallization to be observed during DSC scans. The DSC curve of quenched pure PBN had neither a T_g nor a cold crystallization exotherm, which

is probably due to the rapid crystallization rate of PBN. In fact, several different T_g values have been reported for PBN in the literature, ranging from 41 to 82°C, which is attributed to difficulties associated with obtaining wholly amorphous samples.[19,20]
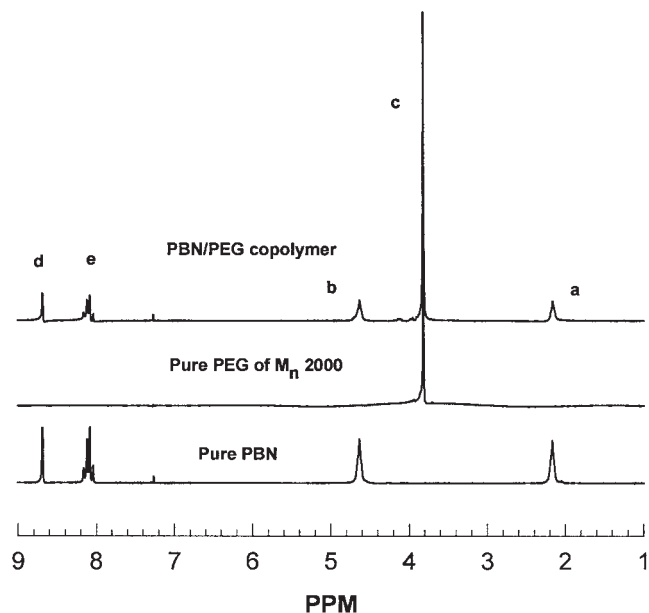
Figure 2 ^{1}H NMR spectra of pure PBN, pure PEG, and PBN/PEG copolymer (PEG of M_n 2000).

Figure 3 DSC curves of PBN/PEG copolymer containing PEGs with different molecular weights.

As shown in Figure 3, the melting temperature (T_m) of pure PBN was 241°C. The BE400–10 and BE900–10 copolymers showed a single melting peak, whereas BE2000–10 and BE3400–10 copolymers had two melting peaks. The higher of these two peaks was ascribed to the PBN (hard segment) and the other to the PEG (soft segment). The T_m's of PBN and PEG in the copolymer were depressed compared with that of pure PBN and PEG. Raquez et al. has reported that T_m of PEG polymers is 50°C for PEG 1500 and 60°C for PEG 4000, respectively.[21]

It is presumed that the PBN and PEG have their preferred crystal phases in the copolymer, and that these crystalline states are formed in BE2000–10 and BE3400–10 copolymers on heating. Thus, the crystal formations of PBN and PEG in copolymers are affected by their mutual presences.
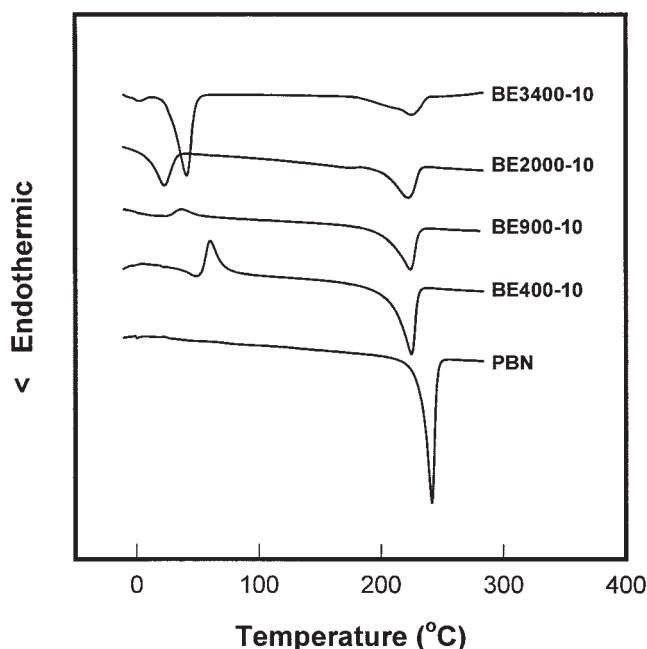
Figure 4 shows the DSC curves of quenched PBN/PEG copolymers containing PEGs with different contents. The T_m of copolymers was depressed from 232°C to 201°C on increasing the PEG content from 5 to 10 mol %. We presume that this decrease is due to increased chain disorder caused by the addition of PEG. In particular, the T_m of BE2000–5 copolymer was 234°C, which was higher than that of the other copolymers.

As shown in Figures 3 and 4, DSC showed that the cold crystallization temperatures (T_{cc}) of BE400–10, BE900–10, BE900–15, and BE900–20 copolymers decreased on increasing content and molecular weight of PEG. We believe that these reductions were due to increased flexibility and mobility of copolymer chains caused by the introduction of flexible PEG chains.

TABLE I
Feed and Copolymer Compositions, and the Intrinsic Viscosities [η] of PBN/PEG Copolymers

Sample codes	PEG M_n (g/mol)	PEG (mol %)		PBN (mol %)		[η] (dL/g)
		Feed composition	Copolymer composition	Feed composition	Copolymer composition	
PBN		0		100	100	0.74
BE400–10	400	10	11.3	90	88.7	0.81
BE900–5	900	5	6.8	95	93.2	0.92
BE900–10	900	10	11.4	90	89.6	1.10
BE900–15	900	15	16.8	85	83.2	1.12
BE900–20	900	20	21.7	80	78.3	1.36
BE2000–5	2000	5	6.0	95	94.0	1.25
BE2000–10	2000	10	12.8	90	87.2	1.48
BE3400–10	3400	10	11.2	90	88.8	1.56

Figure 4 DSC curves of PBN/PEG copolymer containing PEGs with different contents.
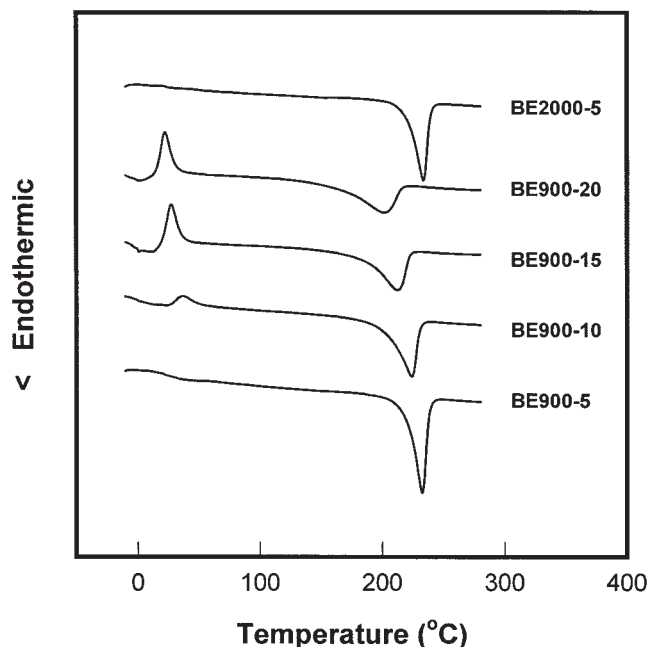

Figure 5 TGA curves of PBN/PEG copolymers containing PEGs with different molecular weights.

Table II shows the thermal transition temperatures of PBN/PEG copolymers, as determined by DSC. As shown in Table II, the heat of fusion (ΔH_f) of pure PBN was 44.9 J/g. Moreover, the ΔH_f's of copolymers reduced on increasing content and molecular weight of PEG, and also because of the influence of PEG component on the crystallization of PBN. In other words, crystals formed in the PBN/PEG copolymers do not form perfect crystalline phases.

TGA was used to investigate the thermal decomposition behaviors of PBN/PEG copolymers. Figure 5 shows TGA curves of PBN/PEG copolymers containing PEGs with different molecular weights. The figure shows that the thermal decomposition temperatures of the copolymers were similar regardless of PEG molecular weights, and that all copolymers showed a single-step thermal degradation. Table III shows the

5% and 50% weight loss temperatures of various copolymers; the 5% and 50% weight loss temperatures of pure PBN are 385 and 415°C, respectively. In the case of BE3400–10 copolymer, its 5% weight loss temperatures were about 6°C lower than that of pure PBN. However, the 5 and 50% weight loss temperatures of all copolymers were similar and fell in the temperature ranges 379–385°C and 419–429°C, respectively, (Table III). The TGA results of the PBN/PEG copolymers produced suggest that the thermal stabilities of these copolymers were relatively unaffected by the incorporation of the PEG into PBN.

Hydrophilic properties

The hydrophilicities of PBN/PEG copolymer films were determined using contact angle and moisture

TABLE II
Thermal Transition Temperatures of PBN/PEG Copolymers Measured by DSC

Sample codes	T_{cc} (°C)	T_m (°C)	ΔH_f (J/g)
PBN	—	241	44.9
BE400–10	60.1	224	31.8
BE900–5	—	232	29.8
BE900–10	36.6	224	24.1
BE900–15	27.1	212	19.7
BE900–20	22.2	201	18.4
BE2000–5	—	233	23.8
BE2000–10	—	222 (22)	17.8 (15.3)
BE3400–10	—	225 (40)	15.2 (35.7)

TABLE III
The 5% and 50% Weight Loss Temperatures of PBN/PEG Copolymers

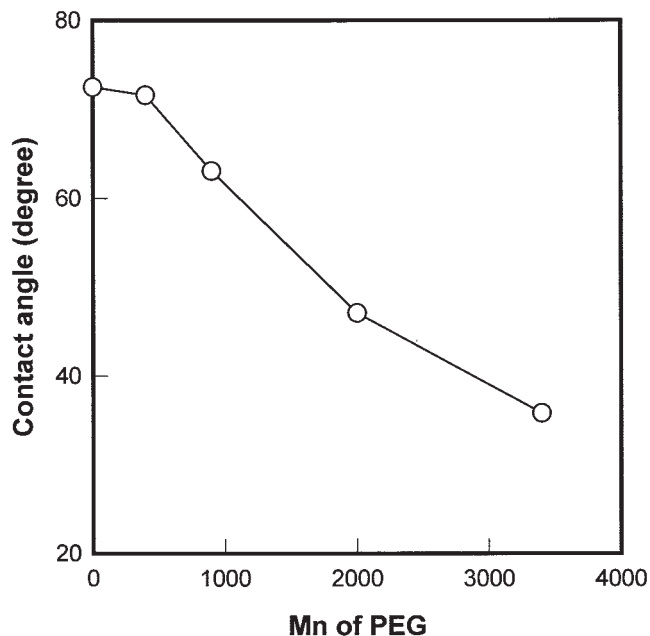| Sample codes	Temp. of 5% weight loss (°C)	Temp. of 50% weight loss (°C)
PBN	385	415
BE400–10	385	419
BE900–5	384	420
BE900–10	385	423
BE900–15	383	424
BE900–20	384	427
BE2000–5	383	423
BE2000–10	381	426
BE3400–10	379	429

Figure 6 Contact angles of PBN/PEG copolymer films containing PEGs with different molecular weights.

content measurements. Figure 6 shows changes in the contact angles of PBN/PEG copolymer films containing PEGs with different molecular weights. As shown in Figure 6, the contact angle of pure PBN and BE400–10 copolymer films were 72° and 71°, respectively, which is in accord with the higher hydrophobicity of pure PBN. The contact angles of BE900–10–BE3400–10 copolymer films ranged from 63 to 35°,
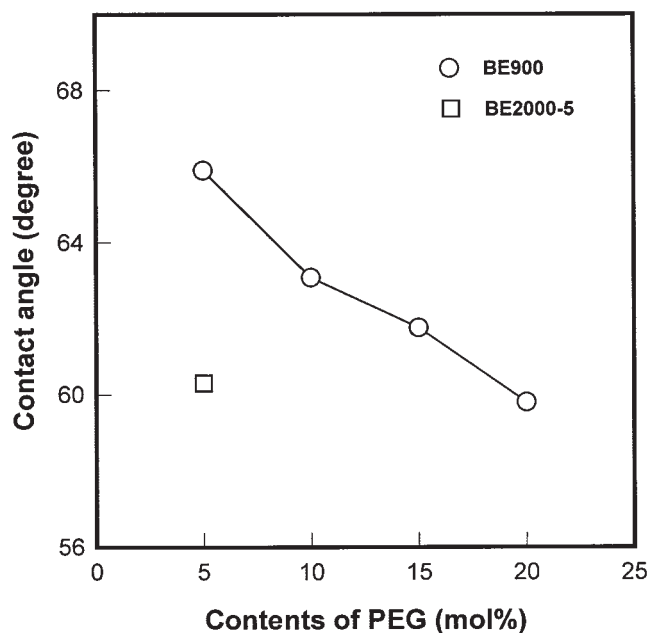

Figure 7 Contact angles of PBN/PEG copolymer films containing PEGs with different contents.
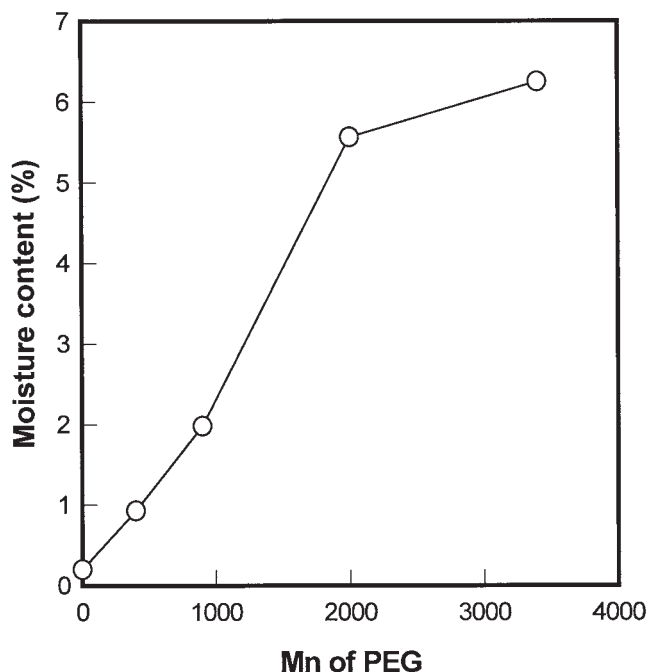

Figure 8 Moisture contents of PBN/PEG copolymer films containing PEGs with different molecular weights.

respectively, and were about 9–37° lower than that of pure PBN, which demonstrates that copolymer film contact angles were much reduced by increasing PEG molecular weights above 900.

Figure 7 shows changes in the contact angles of PBN/PEG copolymer films containing PEGs with different contents (mol %). As the PEG content was increased from 65° to 59°, the contact angles were reduced. In particular, the contact angle of BE2000–5 copolymer was 60°, which is similar to that of BE900–20 copolymer. We presume that PEG of high molecular weight is more distributed on the surface of the copolymer film because PEG mobility is increased on increasing the PEG molecular weight.[14] Thus, our results show that the molecular weight of PEG has a greater influence on hydrophilicity of PBN/PEG copolymer than PEG content.

Our contact angle measurements show that increases in PEG content and molecular weight improve the water affinity of PBN/PEG copolymer.

Figure 8 shows that changes in the moisture contents of PBN/PEG copolymer films containing PEGs with different molecular weights. The moisture contents of pure PBN and BE400–10 copolymer were about 0.2% and 0.9%, respectively, whereas the moisture content of BE900–10 copolymer was 1.9%, which is higher than that of pure PBN. Moreover, this was increased to 6.3% when the molecular weight of PEG was increased from 3400 to 900, which also demonstrates that the moisture contents of these copolymer films are increased by increasing PEG molecular weights.
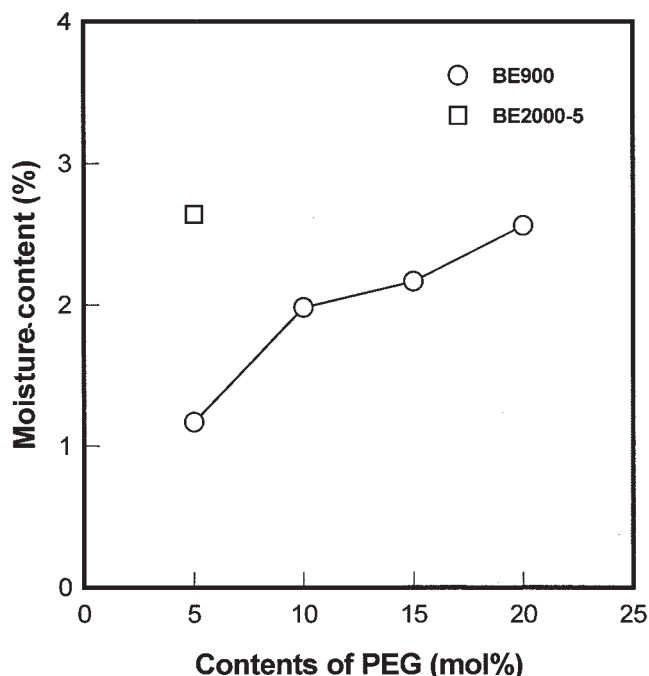
Figure 9 Moisture contents of PBN/PEG copolymer films containing PEGs with different contents.

On the other hand, when the content of PEG was increased from 5 to 20 mol %, the moisture content of the copolymer film increased from 1.1% to 2.5%, as shown Figure 9. The moisture content of BE2000–5 copolymer was 2.6%, which was higher than that of BE900–20 copolymer. Thus, we believe that the hydrophilicity of PBN/PEG copolymer is more markedly affected by PEG molecular weight than PEG content. From the results shown in Figures 6–9, we conclude that hydrophilicities as determined by copolymer film contact angle and moisture content measurements are significantly improved by increasing both the content and the molecular weight of PEG.

CONCLUSIONS

PBN/PEG copolymers were synthesized by the two-step melt copolymerization process of 2,6-NDC with EG and PEG. The effects of PEG contents (mol %) and molecular weights on the thermal properties and hydrophilicities of copolymers were investigated.

We found that the molar ratios of copolymer compositions were approximately the same as that expected from the feed compositions for PEGs of M_n 400–3400 at 5–20 mol %. As PEG contents and molecular weights were increased, the $[\eta]$ values of PBN/PEG copolymers increased, but T_m, T_{cc}, and ΔH_f values decreased.

The thermal stabilities of the copolymers were found to be relatively unaffected by PEG contents or molecular weights.

Water contact angles decreased as did copolymer moisture contents when PEG contents and molecular weights were increased. Thus, we conclude that the hydrophilicity of PBN/PEG copolymer is well fitted by using a small amount of high molecular weight PEG rather than a large amount of low molecular weight PEG.

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