Effect of Dialcohols on Properties of Poly(ethylene 2,6-naphthalate) Copolymers

KWAN HAN YOON,[1] HYUN NAM CHO,[2] O OK PARK[3]

[1] Department of Polymer Science and Engineering, Kumoh National University of Technology, 188, Shinpyung-Dong, Kumi, Kyungbuk 730-701, Korea

[2] Polymer Materials Lab, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

[3] Department of Chemical Engineering, Korea Advanced Institude Science and Technology, 373-1, Kusung-Dong, Yusung-ku, Taejon 305-701, Korea

ABSTRACT: Properties of poly(ethylene 2,6-naphthalate) (PEN) and its copolymers containing diethylene glycol (DEG), propanediol (PD), butanediol (BD), and bisphenol A ethoxylate (BSA) were investigated. The copolymer composition was determined by ^{1}H-NMR spectroscopy. It has a higher value than the feed composition due to the high volatility of ethylene glycol (EG). The melting temperature of the copolymers was gradually depressed with the increase of dialcohol in the composition. The complex viscosity of the copolymers did not depend on the molecular weight, but on the chemical structure. The complex viscosity of the copolymers containing 3 mol % of DEG, BD, and 5 mol % of BD was lower than that of PEN, and the mechanical properties were similar with the value of PEN. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2900–2905, 1999

Key words: poly(ethylene 2,6-naphthalate); copolymer; melting temperature; complex viscosity; mechanical property

INTRODUCTION

Poly(ethylene 2,6-naphthalate) (PEN)[1–7] is quite useful for many packaging applications, due to good mechanical properties, low permeability of oxygen and carbon dioxide, and good thermal properties (high melting and high glass transition temperature), which are generally superior to poly(ethylene terephthalate) (PET). Although PEN has superior physical and mechanical properties than PET, however, its relative low production volume and high price will limit its application.

Blends of PEN and other polyesters should be useful in engineering plastics, if, of course, they are miscible. Unfortunately, the blends of PEN/PET,[8] PEN/poly(butylene naphthalate)[7] (PBN), and PEN/poly(butylene terephthalate) (PBT)[9] have been found to be immiscible or partially miscible. Especially, the larger melting temperature difference between PEN and polyesters containing butanediol (BD) unit may induce the thermal degradation in lower melting temperature component, resulting in the poor mechanical properties of the blends.

For this reason, it was of interest to prepare PEN copolymers. Also, the raw material cost of PEN can be reduced by choosing inexpensive comonomers if the better properties of PEN are maintained. So in this work we compared the properties of PEN copolymers by incorporation of small amounts of alcohols such as diethylene glycol (DEG), propanediol (PD), butanediol (BD), and

bisphenol A ethoxylate (BSA) into the polymer composition to maintain the mechanical properties of PEN. The thermal and mechanical properties as well as complex viscosity of PEN copolyesters were investigated.

EXPERIMENTAL

Polymer Preparation

PEN was prepared by melt polycondensation. Dimethyl naphthalate (DMN) was reacted in a nitrogen environment with ethylene glycol (EG) in the presence of a titanium isopropoxide catalyst in a small-scale batch reactor. The reactor was first heated to 190°C in a silicone oil bath. This temperature was maintained for 2 h. After that, the temperature was increased to 210°C, and maintained for 2 h. The reaction temperature was progressively increased to 280°C. Then the pressure was reduced to a specified level and maintained for 0.5–1 h. PEN copolyesters containing 3–10 mol % diethylene glycol (DEG), propanediol (PD), butanediol (BD), and bisphenol A ethoxylate (BSA) were prepared by the same procedure.

Measurements

To determine the amount of dialcohol incorporated into PEN, a 200-MHz FT-NMR spectrometer (Bruker AMX-200) was used. The mixed solvents used were deuterated trifluoroacetic acid/chloroform (70/30, v/v). The weight-average molecular weight of PEN and its copolymers was measured by light-scattering methods. The intrinsic viscosity was measured by mixed solvent of phenol/tetrachloroethane (60/40, v/v) at 35°C. Thermal analysis was performed on a du Pont 910 differential scanning calorimeter (DSC), and all scans were conducted at 20°C min^{-1}. Rheological properties (complex viscosity) were measured with frequency at 280°C by Physica, Rheo Lab MC 120. The tensile properties, such as the tensile strength at yield and the initial modulus measured at 0.2% elongation, were measured using an Instron model 4467 universal instrument. Measurements were made at room temperature at a constant crosshead speed of 2 mm min^{-1} on specimens that were made by Mini Max Molder (CS-183 MMV-203). Data were taken as averages of at least five measurements.
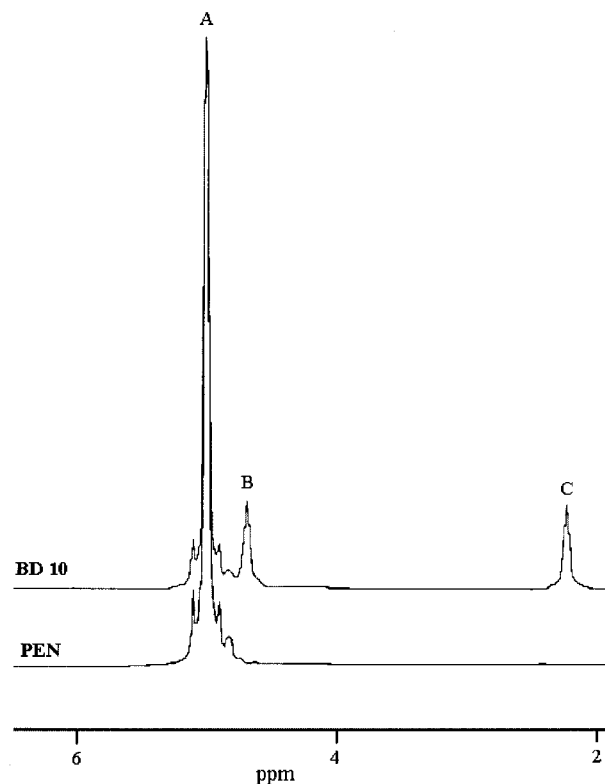
Figure 1 ^{1}H-NMR spectra of PEN and the copolymer containing BD10.

RESULTS AND DISCUSSION

Copolymer Composition

The composition of PEN copolymer containing BD10 was determined from ^{1}H-NMR, as shown in Figure 1. Three main peaks were used for this determination: one for the ethylene unit (A: 4.9 ppm) and two for the butylene unit (B: 4.81 ppm; C: 2.21 ppm). Thus, the molar composition of BD was found using the following equation:

$$BD \ (mol \ \%) = A/(A + D) \times 100$$

where D = (B + C)/2.

The compositions of dialcohols reacted during polymerization were determined through this method to compare with the initial amount of dialcohols introduced into the reaction. The results are listed in Table I. It can be seen from these results that the actual molar composition is higher than that of the feed composition. Such a discrepancy was also reported[10] for copolymers prepared from DMN, EG, and 1,6-hexanediol. It is worth noting that EG has a lower boiling point

Table I   Properties of PEN and Its Copolymers

| Materials | Feed Composition (mol %) | | Intrinsic Viscosity[a] (dL/g) | Dialcohols Content[b] (mol %) | Molecular Weight[c] (M_w) |
	EG	Relative Dialcohols			
PEN	100	0	0.56	—	33,800
DEG3[d]	97	3	0.58	3.8	34,200
DEG5	95	5	0.58	5.1	44,100
DEG7	93	7	0.61	5.9	40,700
DEG10	90	10	0.51	13.2	33,500
PD3	97	3	0.55	5.1	32,500
PD5	95	5	0.53	5.8	43,100
PD7	93	7	0.48	10.4	28,000
PD10	90	10	0.51	15.5	29,500
BD3	97	3	0.53	4.7	31,700
BD5	95	5	0.50	7.3	26,900
BD7	93	7	0.54	9.6	30,700
BD10	90	10	0.51	13.1	36,800
BSA3	97	3	0.56	6.0	35,900
BSA5	95	5	0.60	9.1	36,200
BSA7	93	7	0.63	12.5	37,600
BSA10	90	10	0.67	16.7	25,700

[a] Values measured by mixed solvent of phenol/tetrachloroethane (60/40, v/v) at 35°C.
[b] Values measured by ^{1}H-NMR.
[c] Values measured by light scattering.
[d] It indicates the initial amount of dialcohols introduced into the reaction.

(198°C) compared to those of BD (230°C), DEG (245°C), and PD (214°C). The difference between copolymer and feed composition could find its origin in polymerization process, when bis-hydroxyalkyl naphthalates are condensated with concurrent evolution of an EG or other dialcohols. The evolution of EG should occur more readily than that of dialcohols, due to its higher volatility, enriching the copolymer composition with alkylene units.
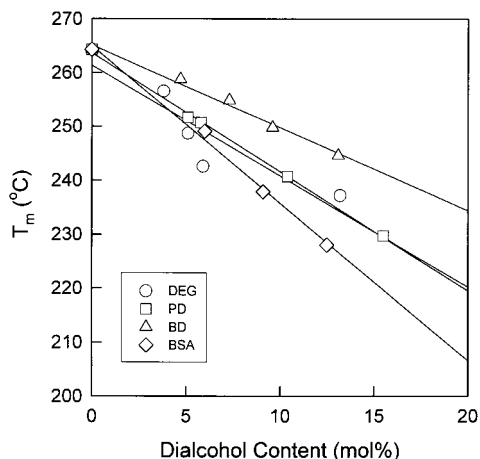
Thermal Properties

DSC thermograms of the quenched PEN copolymers containing BD are shown in Figure 2. A single melting temperature (T_m) was observed, depending on the BD contents. DSC thermograms of PEN copolymer containing various dialcohols compositions were analyzed, and their T_m and glass transition temperature (T_g) behaviors are shown in Figures 3 and 4, respectively. T_m values decreased linearly with the dialcohols composition except for copolymers containing DEG.

Using the theory of melting temperature depression of copolymers, the heat of fusion (ΔH_f) of PEN can be calculated from the copolymer melt-

ing temperatures. According to the theory, the component that brings about the depression in T_m of a polymer may be a constituent of the polymer itself. In a copolymer consisting of A units that crystallize and B units that do not, the latter should depress the melting temperature of the former according to Flory's equation:[11]
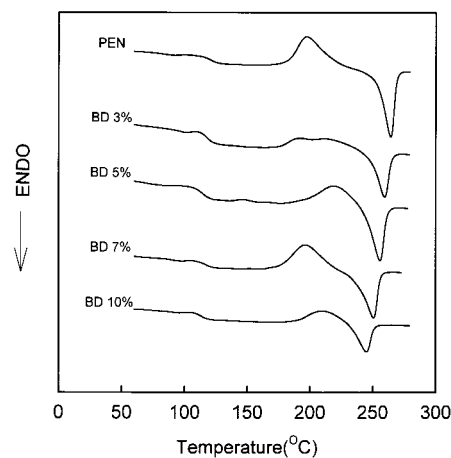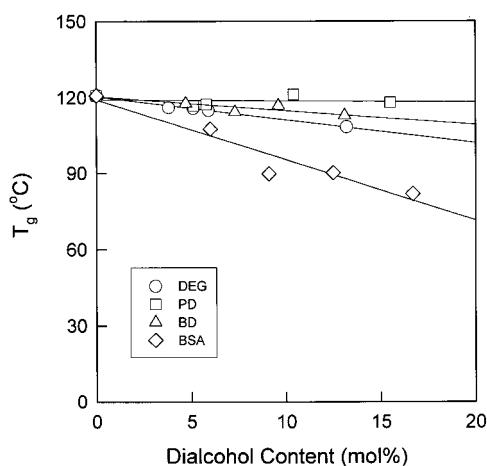

Figure 2   DSC curves of the quenched PEN and the copolymers containing BD.
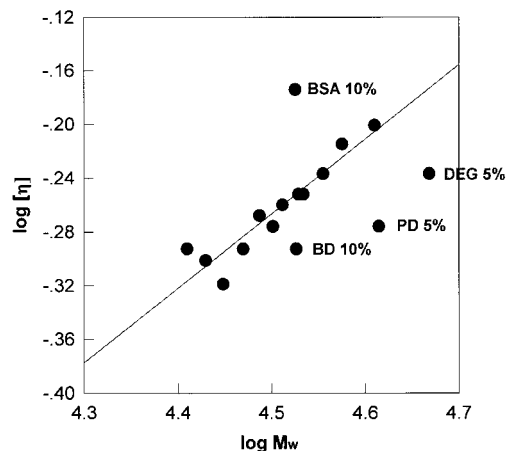
Figure 3 Melting temperature of the copolymers as a function of dialcohol content.

Figure 5 Plot of log [η] vs. log M_w measured by light scattering for PEN and its copolymers.

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\left(\frac{R}{\Delta H_f}\right) \ln X_A$$

where T_m and T_m° are the melting temperatures at the molar fraction (X_A) corresponding to random copolymers and the homopolymer, respectively. R is the gas constant (8.314 J/ mol), and ΔH_f is the heat of fusion per repeating unit of homopolymer with A units. If this equation is applied for the copolymers, $R/\Delta H_f$ values were obtained from the slope of the $1/T_m$ vs. $\ln X_A$ plot. The heats of fusion calculated were 11.5 kJ/mol from PD, 14.5 kJ/mol from BD, and 7.4 kJ/mol from BSA for PEN. The theoretical value of ΔH_f was calculated as 25 kJ/ mol for PEN by the group contribution method.[12] Such discrepancies between the theoretical val-

ues of ΔH_f and those determined based on the above equation of Flory were attributed to the dependence of T_m depression not on the molar fraction X_A but, rather, on the sequence propagation probability.

Figure 4 shows the glass transitions of PEN copolymers containing various dialcohols with the content of dialcohols. The T_gs of the copolymers containing PD, BD, and DEG are constant or slightly decrease with their dialcohol compositions. However, the T_g of BSA copolymer decreases considerably. It is believed that BSA has a larger and more flexible unit than other dialcohols. The increased flexible dialcohol content of copolymers will result in a reduced packing density, hence, in lower T_g values.

Figure 4 Glass transition temperature of the copolymers as a function of dialcohol content.
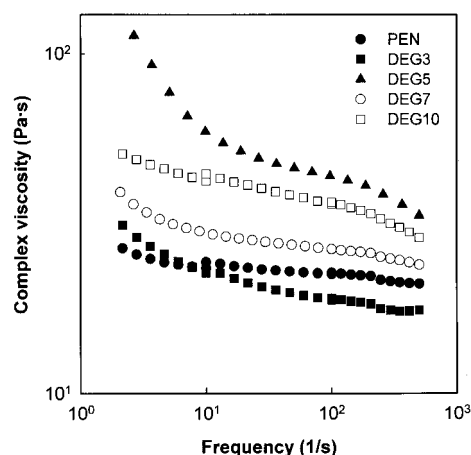
Figure 6 Complex viscosity of PEN and its copolymers containing DEG with a frequency at 280°C.
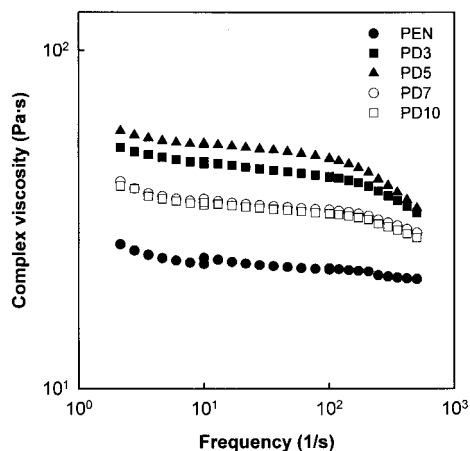
Figure 7 Complex viscosity of PEN and its copolymers containing PD with a frequency at 280°C.
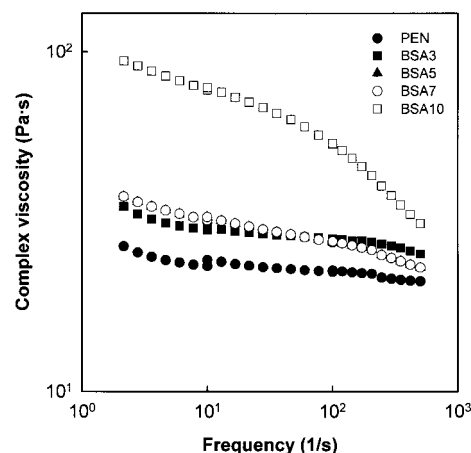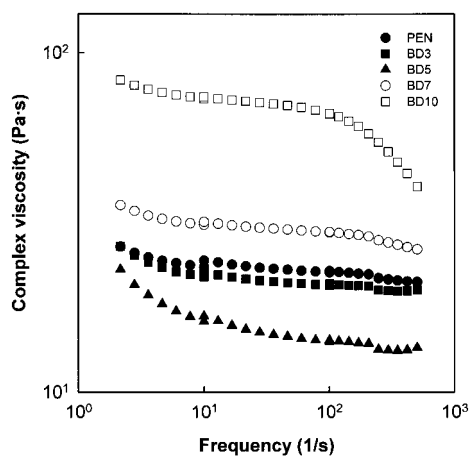

Figure 9 Complex viscosity of PEN and its copolymers containing BSA with a frequency at 280°C.

Molecular weight and Viscosity

Figure 5 shows the relationship between the intrinsic viscosity $[\eta]$ and the weight-average molecular weight (M_w), which was determined by light scattering. Except for DEG5, PD5, BD10, and BSA10 copolymers, the linearity is obtained. The deviation from linearity in light-scattering measurement results from the different chemical structure, i.e., randomness.

Figures 6–9 show the complex viscosity of PEN and its copolymers containing DEG, PD, BD, and BSA with a frequency at 280°C. Complex viscosity depends on the molecular weight and the chemical structure. For the complex viscosity of the DEG copolymer as shown in Figure 6, there is no dependence on the molecular weight. Except

for DEG3, copolymers have a higher viscosity than that of PEN. This may result from the different chemical structures. Figure 7 shows the complex viscosity of the PD copolymers. The viscosity of the copolymers is higher than that of PEN, and the dependence of the molecular weight is not observed. In the case of the BD copolymers shown in Figure 8, the viscosities of BD3 and BD5 are lower than that of PEN, whereas BD7 and BD10 have higher viscosities. For copolymers containing BSA shown in Figure 9, copolymers have a higher viscosity than PEN. In all copolymers there was no observed relationship between the complex viscosity and the molecular weight. It is interesting to note that the copolymers having the highest viscosity in each copolymer series devi-

Figure 8 Complex viscosity of PEN and its copolymers containing BD with a frequency at 280°C.
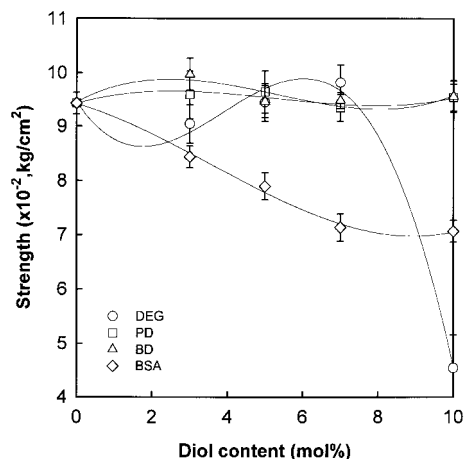
Figure 10 Tensile strength of copolymers with the content of dialcohols at yield.
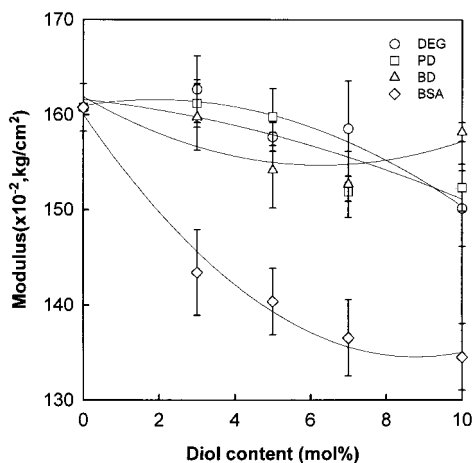
Figure 11 Initial modulus of copolymers with the content of dialcohols at 0.2% of elongation.

ated from the linearity between $[\eta]$ and M_w measured by light scattering, as shown in Figure 5. It is thought that this may result from the different randomness.

Mechanical Properties

The tensile strength at yield and initial modulus at 0.2% elongation were measured and shown in Figures 10 and 11, respectively. In the case of the copolymers containing PD and BD, the tensile strength is almost constant with their composition, whereas in the case of BSA, it decrease continuously with the content. Especially, the copolymer having DEG has almost the same tensile strength value up to 7 mol %, but that of 10 mol % drops abruptly. For the modulus, the value of the copolymer containing BSA decreases continuously with the content of BSA, whereas other copolymers show the behaviors decreasing slightly with the content of those. Copolymerization greatly reduces the degree of crystallinity, which brings about decreases in modulus and strength. So we measured the degree of crystallinity of the tensile specimen of copolymers through DSC curve. Except for BSA copolymers and DEG10, the degree of crystallinity was within the range of 8–10%.

CONCLUSIONS

We tried to find the copolymer composition that does not affect the mechanical properties but decreases the melting temperature of poly(ethylene 2,6-naphthalate) (PEN) by incorporation of small amounts of dialcohols such as diethylene glycol (DEG), propanediol (PD), butandiol (BD), and bisphenol A ethoxylate (BSA). The results are as follows.

1. In terms of complex viscosity, the copolymers containing DEG3, BD3, and BD5 showed a lower viscosity than that of PEN.
2. The tensile strength of the copolymers, except for DEG10 and BSA copolymers, showed a similar value with PEN.
3. The initial modulus of copolymers containing 3 mol % dialcohol, except for BSA3, showed a similar value with PEN.
4. The melting temperature of copolymers linearly decreases with their dialcohol content except for the DEG copolymer.

REFERENCES

1. Cook, J. G.; Huggill, H. P. W. BP 604073 (1948).
2. Quchi, I.; Aoki, H.; Shimotsuma, S.; Asai, T.; Hosoi, M. Proc 17th Japan Congr Materials Research 1974.
3. Anon. Res Disclosure 29428 (1988).
4. Lee, S. C.; Yoon, K. H.; Park, I. H.; Kim, H. C.; Son, T. W. Polymer 1997, 38, 4831.
5. Yoon, K. H.; Lee, S. C.; Park, I. H.; Lee, H. M.; Park, O. O.; Son, T. W. Polymer 1997, 38, 6079.
6. Yoon, K. H.; Lee, S. C.; Park, O. O. Polym Eng Sci 1995, 35, 1807.
7. Yoon, K. H.; Lee, S. C.; Park, O. O. Polym J 1994, 26, 816.
8. Guo, M.; Zachman, H. G. Polymer 1993, 34, 2053.
9. Yoon, K. H.; Lee, S. C.; Park, O. O. Korea Polym J 1994, 2, 75.
10. Park, S. S.; Kim, I. K.; Im, S. S. Polymer 1996, 37, 2165.
11. Flory, P. J. Trans Faraday Soc 1955, 51, 848.
12. Baker, C. H.; Mandelkern, L. Polymer 1966, 7, 7.