Structural and Physical Properties of Biodegradable Copolyesters from Poly(ethylene terephthalate) and Polycaprolactone Blends

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ABSTRACT: The relationship between the degree of ester-interchange reactions and the physical properties in the melt blending of poly(ethylene terephthalate) (PET) and polycaprolactone (PCL) was investigated in terms of the blending time. ^{1}H-NMR and ^{13}C-NMR spectra confirmed that poly-(ethylene terephthalate caprolactone) copolyesters were generated and became dominant at a blending time of more than 15 min, and this result may be related to the degree of the thermal decomposition of PCL. The spectra disclosed the effect of the blending time on the block characteristics of the ethylene terephthalate (ET) and caprolactone (CL) units of the copolyesters. The melting temperatures and heats of fusion assigned to the ET units in the copolyesters decreased with the blending time. However, the melting peak of the CL units disappeared when the blending time exceeded 20 min. For the CL block, the number of the average repeating units (5) proved to be the least critical value for crystallization. The crystallinity of the copolyesters was most notably reduced with a blending time up to 20 min. The total organic carbon (TOC) content of the copolyesters, a quantitative measure of biodegradability, increased steeply with the blending time up to 20 min. However, the TOC content increased slowly during extended blending. This agrees well with the recognized fact that the accession and penetration of lipase into copolyesters initiate in the amorphous region of the polymer. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 131–138, 2003

Key words: polyesters; blending; biodegradable

INTRODUCTION

Poly(ethylene terephthalate) (PET) has been widely used in the fiber, sheet, and film industries. However, its wastes may cause environmental problems, although PET can be partially recycled.[1–3] One of the possible solutions for these problems may be the use of biodegradable polymers. Recently, biodegradable copolyesters have attracted much attention because of their good biodegradability and melt processibility.[4–8] They are generally prepared by the incorporation of biodegradable units such as aliphatic esters into the PET backbone by ester-interchange reactions as follows. Two preparative methods are polycondensation based on molecular design and the reactive melt blending of different polyesters. In polycondensation, cyclized dimers and an aliphatic diol or aliphatic dicarboxylic acid are frequently added to the polymerization of PET.[9–13] Recently, numerous articles have been published on melt-blending systems because of the simpler process and easier control over composition.

However, understanding the block characteristics of copolyesters influenced by the degree of ester-interchange reactions in melt blending is very important because they have a decisive effect on the physicochemical properties. In addition, biodegradable copolyesters require a good combination of biodegradability and mechanical properties, which depend on the degree of ester-interchange reactions. It is well recognized that biodegradability is greatly affected by crystallinity. Therefore, a higher crystallinity reduces biodegradability because a hydrolytic attack by an enzyme initiates in the amorphous region of a polymer.[3,14–16] There have been numerous reports of the effects of biodegradable unit contents on the degradation behavior of copolyesters.[17–19] However, there have been few reports on the relationship between biodegradability and crystallinity as a function of the block characteristics of copolyesters at a given blend composition.

In this study, we attempted to control the block characteristics of copolyesters by varying the blending time in the melt blending of PET and polycaprolactone (PCL). In this case, the procedure must be accomplished within a short time because of the poor thermal stability of PCL. This frequently raises the prob-

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lem of the immiscibility between PET and PCL due to the lack of ester-interchange reactions. In addition, a longer blending time gives rise to poor mechanical properties for the resultant copolyesters because of the decrease in the molecular weight. Therefore, control over the blending time may be of great technical importance for the miscibility of PET and PCL and for the mechanical properties of the resultant copolyesters formed by ester-interchange reactions.

The principal objective of this study was to investigate the relationship between the degree of ester-interchange reactions and the physicochemical properties in the melt blending of PET and PCL. The kinetics of the ester-interchange reactions were characterized, and the thermal properties and morphology of the resultant compounds were examined as well.

EXPERIMENTAL

Materials

PET [weight-average molecular weight (M_w) = 18,000] and PCL (M_w = 80,000) were supplied by Korye Corp. (Korea) and Union Carbide Corp. (USA), respectively. Reagent-grade tetrahydrofuran (THF), d-trifluoroacetic acid, and CDCl$_3$ were used as received without further purification. *Rhizopus arrihizus* lipase and the surfactant Plysulf A210G were purchased from Boehringer Mannhein Corp. (Germany) and Daiichi Kogyo Seiyaku Corp. (Japan), respectively.[7,17–18] PET/PCL blends were prepared by melt blending in a Haake mixer at 285°C for 5, 10, 15, 20, 30, 40, 50, and 60 min. The blending ratio was fixed at PET/PCL = 62.7/37.3 (w/w), which corresponds to a 1/1 molar ratio of repeating units.

Characterization of the blend systems

^{1}H-NMR and ^{13}C-NMR spectra were obtained with a Varian Gemini 200 200-MHz spectrometer (United States) with a 1/1 (v/v) d-trifluoroacetic acid/CDCl$_3$ mixture as the solvent. The differential scanning calorimetry (DSC) curves were obtained with a TA Instruments DSC 2100 (United States) at a scanning rate of 10°C/min under nitrogen purging. The morphology of the blends was observed with scanning electron microscopy (SEM; ABT SX-40A, Japan). The SEM samples were prepared by cryofracture with liquid nitrogen, followed by the etching of the fractured surface in THF for 1 min for the elimination of the PCL component. The molecular weight was measured by gel permeation chromatography (GPC; Waters Co.) with hexafluoroisopropanol (0.2% w/v) as the solvent at 23°C, the calibration curve of which was obtained with monodisperse polystyrene. For the evaluation of the biodegradability of the blends, the samples were hydrolyzed by *R. arrihizus* lipase. A mixture containing
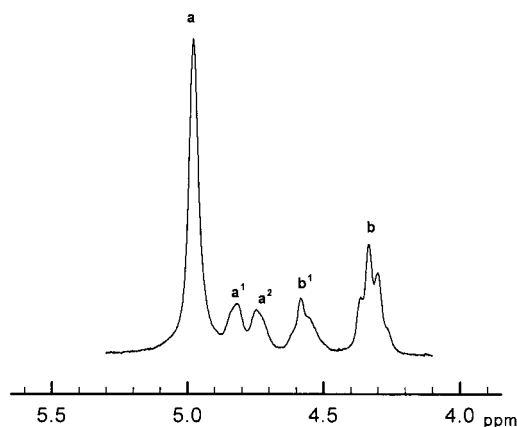
Figure 1 ^{1}H-NMR spectrum of a PET/PCL (62.7/37.3 w/w) blend (blending time = 60 min): (a) EG unit and (b) CL unit. The new peaks (a^1, a^2, and b^1) are assigned to hydrogen on methylene groups adjacent to ester oxygen.

300 mg of a film blend sample, 1 mg of the surfactant Plysulf A210G, 1 mg of the lipase, and 10 mL of a phosphate buffer was incubated at 37°C for 10 days.[7] The mixture was filtered so that the total organic carbon (TOC) could be measured, which was converted to the TOC value according to the weight of the sample for an estimation of the biodegradability. The TOC content was measured on a TOC analyzer (TOC-5000A, Shimadzu, Japan).

RESULTS AND DISCUSSION

Characterization of the ester-interchange reactions

Figure 1 shows the ^{1}H-NMR spectrum of a PET/PCL blend prepared by melt blending at 285°C for 30 min. Peaks a and b at chemical shifts of 4.98 and 4.32 ppm are assigned to the ethylene glycol (EG) unit of PET and the —CO—O—CH$_2$— unit of PCL, respectively. The new peaks a^1, a^2, and b^1 appear around 4.98–4.32 ppm. They are assigned to the methylene hydrogen adjacent to the ester group, the environment of which is different from those in PET and PCL. Therefore, peaks a^1 and a^2 are assigned to an EG—caprolactone (CL) unit link, and peak b^1 is assigned to a terephthalic acid (TA)—CL unit link, as described in Table I.[20–23] Consequently, the appearance of these new peaks on the ^{1}H-NMR spectrum suggests that a poly(ethylene terephthalate caprolactone) P(ET/CL) [P(ET/CL)] copolyester is indeed formed through ester-interchange reactions during melt blending.

The molecular structure of the P(ET/CL) copolyester can also be characterized by ^{13}C-NMR analysis. Figure 2 shows the ^{13}C-NMR spectra of PET, PCL, and a P(ET/CL) copolyester prepared by melt blending at 285°C for 30 min. Peaks 1 and 4 at chemical shifts of 174.8 and 164.5 ppm are assigned to the carbonyl groups of PET and PCL, respectively. Peaks 6 and 7 at

TABLE I
Chemical Structures Possible in P(ET/CL) Copolymers Showing the Chemical Environment of the Methylene Groups and Ester Carbons, Which Have Different Chemical Shifts in ^{1}H-NMR and Spectra

Bond species	Chemical structure
–TA–EG–	
–EG–CL–	
–TA–CL–	
–CL–CL–	

The numbers in parentheses designate the peaks in Figures 1 and 2.

chemical shifts of 61.9 and 51.8 ppm are assigned to the carbons adjacent to the ester oxygens of PET and PCL, respectively. The new peaks 2, 3, 5, and 8 appear around the peaks of PET and PCL. If the PET/PCL blend is merely a physical mixture formed in the absence of ester-interchange reactions, only peaks 1, 4, 6, and 7, assigned to PET and PCL homopolymers, should be detected. Therefore, the new peaks of the ^{13}C-NMR spectrum suggest the existence of four types of ester links of the P(ET/CL) copolyester chain. The P(ET/CL) copolyesters are composed of new ester links (—TA—CL— and —EG—CL—) formed by ester-interchange reactions as well as ester links (—TA—EG— and —CL—CL—) of PET and PCL homopolymers (Table I).

Figure 3 shows the ^{1}H-NMR spectra of PET/PCL blends at various blending times. The numbers represent the ratios (%) of each peak area to the total peak area. At longer blending times, the areas of peaks assigned to the EG units and the —CO—O—CH$_2$— unit of CL units tend to decrease, but the area ratio of new peaks tends to increase. The area ratio of the peak assigned to the TA unit remains constant. In the samples for which the blending time is less than 10 min, new peaks are not so noticeable, but the peaks become obvious as the blending time exceeds 15 min. This agrees with the fact that ester-interchange reactions do not occur significantly at blending times of less than 15 min.

However, the other influencing factor on the ester-interchange reactions during melt blending may include the thermal decomposition of PCL. Therefore, a PCL homopolymer may be decomposed into PCL diols or derivatives with low molecular weights at a high blending temperature. This gives rise to an increase in the amount of hydroxyl end groups and subsequently increases the degree of ester-interchange reactions because alcoholysis is kinetically faster than acidolysis and direct transesterification.[24–26] The importance of the role of alcoholysis by hydroxyl end groups via the control of the molecular weight of PET in the kinetics of the ester-interchange reactions between PET and poly(ethylene naphthalene-2,6-dicarboxylate) is reconfirmed.[27–29] As shown in Figure 4, the rate of thermal decomposition of PCL at 285°C increases steeply from about 15 min. This result is agrees with the degree of ester-interchange reactions determined from ^{1}H-NMR spectra. It suggests that the degree of ester-interchange reactions in the melt
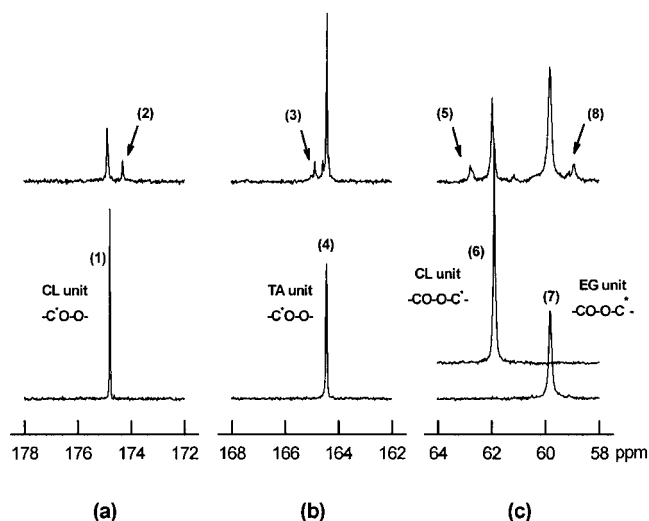
Figure 2 ^{13}C-NMR spectra of PET, PCL, and a PET/PCL (62.7/37.3 w/w) blend (blending time = 30 min): (a) caproate carbonyl carbon, (b) terephthalate carbonyl carbon, and (c) carbon adjacent to ester oxygen.
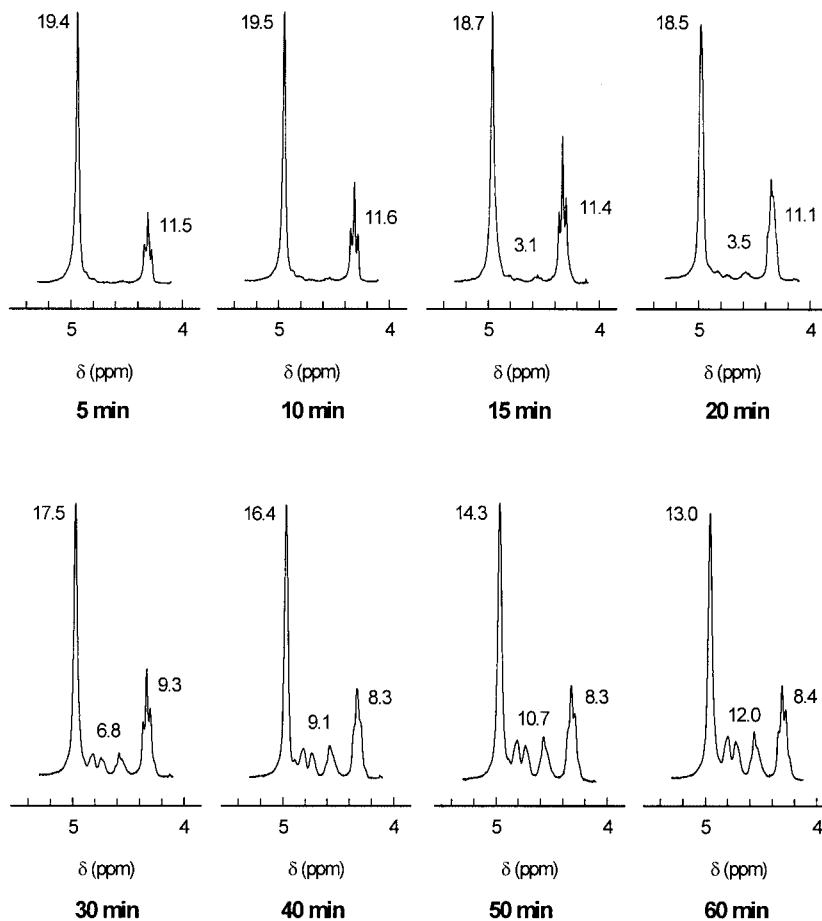
Figure 3 ^{1}H-NMR spectra of PET/PCL (62.7/37.3 w/w) blends with the blending time.

blending of PET and PCL can also be affected by the occurrence of thermal decomposition of PCL.

Structural characteristics

In general, the block characteristics of copolyesters can be determined from the dyad or triad sequence distri-

Figure 4 TGA curve of PCL at 285°C.

bution on the basis of the peak area of the ^{1}H-NMR spectrum.[27,30–32] In this case, a new peak, which is the evidence of ester-interchange reactions, appears only at the intermediate chemical shift. For P(ET/CL) co-polyesters, however, it is difficult to obtain information about the block characteristics due to three new peaks, as shown in Figure 1.

In this study, the numbers of the average repeating units of ethylene terephthalate (ET) and CL blocks, m and n, in the copolyester chain is obtained from the variation of the peak area assigned to the EG unit, X_{EG}, which is calculated as follows:

$$X_{EG} = \frac{A_{TA} - A_{EG}}{A_{TA}} \quad (1)$$

where A_{TA} and A_{EG} are the areas of peaks assigned to TA and EG units, respectively. X_{EG} means the molar fraction of EG units, the environment of which is different from that of the PET homopolymer. The increase in X_{EG} corresponds to the decrease in the ET sequence length in the copolyester chain. Therefore, m can be calculated as follows:
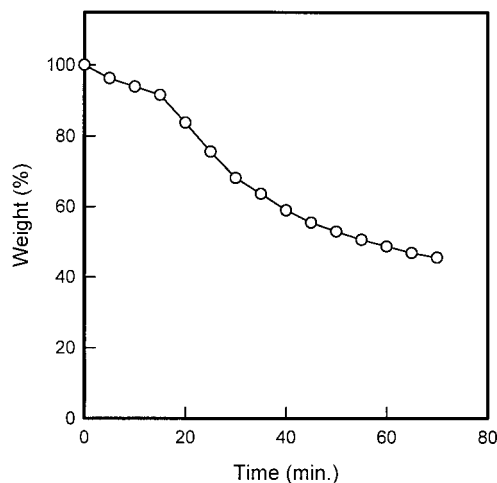
$$m = \frac{1}{X_{EG}} \quad (2)$$

However, the molar fraction of CL units in the copolyesters, X_{CL}, is expressed by eq. (3), and it can be rearranged into eq. (4) in terms of n:

$$X_{CL} = \frac{n}{n + m} \qquad (3)$$

$$n = \frac{m \times X_{CL}}{1 - X_{CL}} \qquad (4)$$

Figure 5 shows the dependence of the number of the average repeating units of ET and CL blocks on the blending time, as calculated by eqs. (2) and (4). The number of the average repeating units of ET and CL blocks decreases with an increasing blending time, and the sequence distribution of the copolymers appears to be random at prolonged blending times. That is, the number of the average repeating unit of ET and CL blocks decreases sharply up to a blending time of 50 min, after which an equilibrium is reached when the number of the average repeating unit is about 3. The number of the average repeating unit of samples blended for 5 and 10 min could not be analyzed because there is little change in the ^{1}H-NMR spectra.
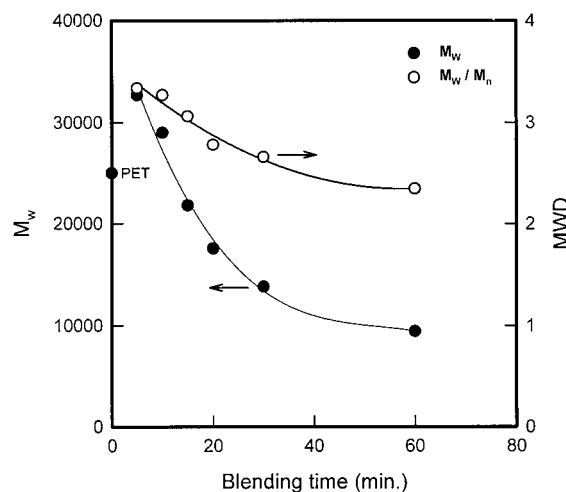
Figure 6 shows the M_w and molecular weight distribution (MWD) of PET/PCL blends determined from GPC. At the longer blending time, M_w and MWD of the blends tend to decrease. In addition, the M_w values of samples blended more than 20 min decrease steeply in comparison with that of PET. This suggests that the melt blending of PET and PCL may be accomplished within 15–20 min.

Thermal properties

Figure 7 (A,B) shows the melting and crystallization behavior of PET/PCL blends with the blending time,
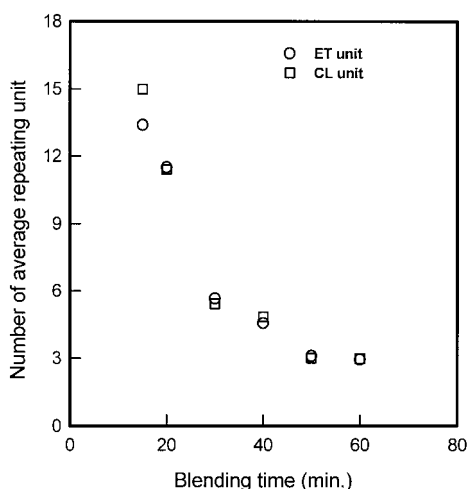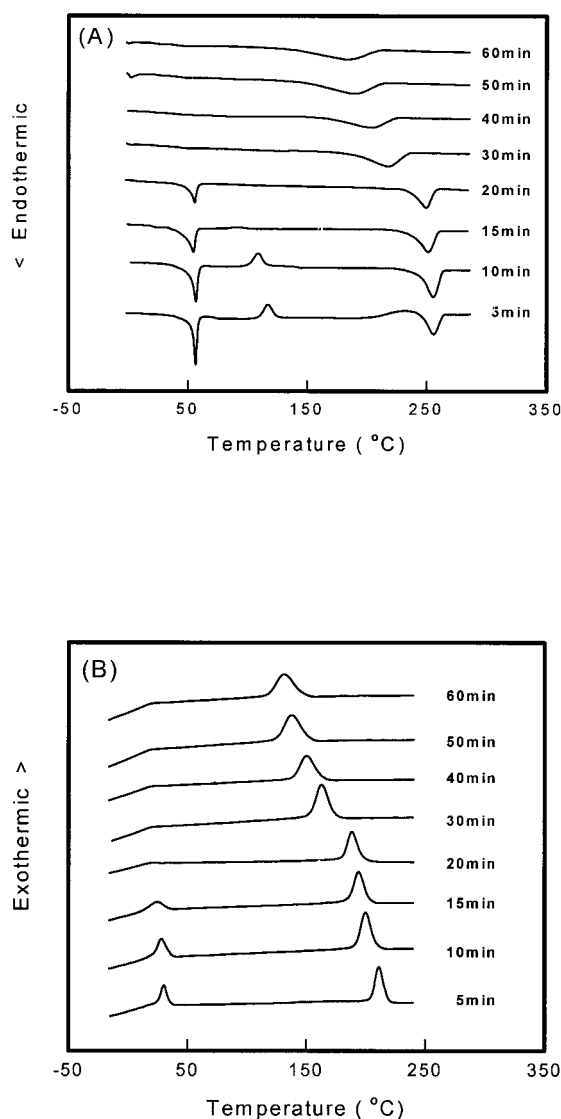

Figure 6 Variation of M_w and MWD of PET/PCL blends with the blending time (PET/PCL = 62.7/37.3 w/w).

respectively. The samples blended less than 20 min exhibit a double melting behavior reflecting the ET and CL blocks. However, at a blending time of more than 30 min, the PET/PCL blends exhibit only the melting behavior of the ET block. With respect to the melting behavior of the copolymers, it is necessary to postulate that a 20–30-Å sequence length of the crystallizable units is a prerequisite for crystallization.[33] For a sample blended less than 20 min, ET and CL blocks are long enough to allow the crystallization of their respective blocks. At blending times greater than 30 min, the ET block, for which the number of the average segment length is greater than 3, can crystallize because the sequence length is more than 30 Å, but the CL block cannot crystallize when the number of the average repeating unit is smaller than 6. In the case of crystallization, the samples blended less than 15 min exhibit a double behavior reflecting the coexistence of ET and CL blocks. At a blending time greater than 20 min, the PET/PCL blends exhibit only the crystallization behavior of the ET block. This indicates that the decrease in the sequence length restricts the crystallization and reduces the crystal size.

Figure 8 shows thermogravimetric analysis (TGA) curves of PET/PCL blends at various blending times. All the samples exhibit a similar decomposition behavior. In addition, they have good thermal stability up to 350°C, which indicates that the copolyesters prepared by the melt blending of different polyesters possess similar thermal stabilities, regardless of the block characteristics.

Figure 5 Number of the average repeating unit for ET and CL blocks versus the blending time (PET/PCL = 62.7/37.3 w/w).

Solubility tests

Figure 9 shows the variation of the weight ratio of THF-soluble and THF-insoluble fractions of PET/PCL blends with the blending time. At blending times of
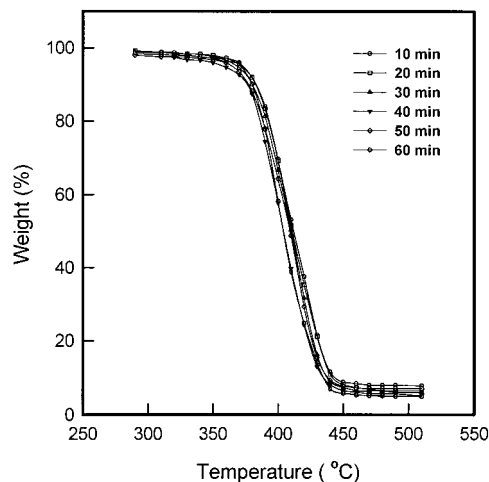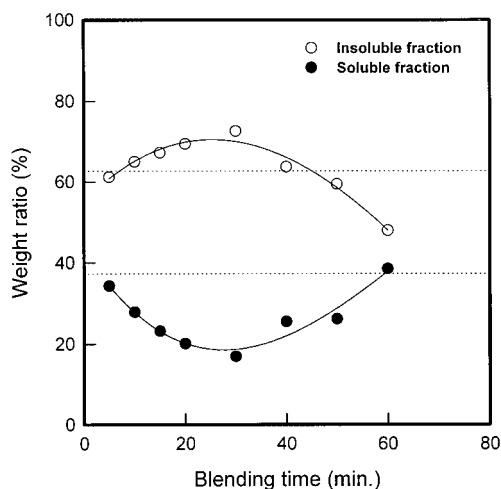
Figure 8 TGA curves of PET/PCL (62.7/37.3 w/w) blends with the blending time.

times. The soluble fractions are assumed to be the pure PCL component unreacted with PET or the copolymers including a long CL block or randomly structured copolymers composed of a short block. In the samples for which the blending time is less than 30 min, the dissolved component produces craters. However, the craters disappear at prolonged blending times, and finally the morphology of the copolymer changes into a continuous single phase, suggesting the variation of solubility as shown. This also indicates that the copolymer converts from a heterogeneous block copolymer into a homogeneous random copolymer with increasing blending time because the degree of ester-interchange reactions increases.

Biodegradation behavior

The biodegradability of a polymer is very dependent on the polymer morphology. For copolyesters pre-

Figure 7 Thermal behavior of PET/PCL blends with the blending time: (A) melting and (B) crystallization (PET/PCL = 62.7/37.3 w/w).

less than 30 min, the weight ratio of the soluble fraction decreases, but that of the insoluble fraction increases. This occurs because these copolyesters are formed by the incorporation of a short CL block into a sufficiently long ET block. It also suggests that ester-interchange reactions occur in samples blended for 5 and 10 min, although they are not detected by ^{1}H-NMR. However, for the samples blended more than 30 min, this is not detected by an exhibited reverse tendency. This variation of solubility may result from the fact that the block distribution and length of copolyesters are more random and shorter with increasing blending time.

Morphology

Figure 10 shows SEM micrographs of the THF-etched surfaces of PET/PCL blends at various blending

Figure 9 Variation of the weight ratio of THF-soluble and THF-insoluble fractions of PET/PCL (62.7/37.3 w/w) blends with the blending time.
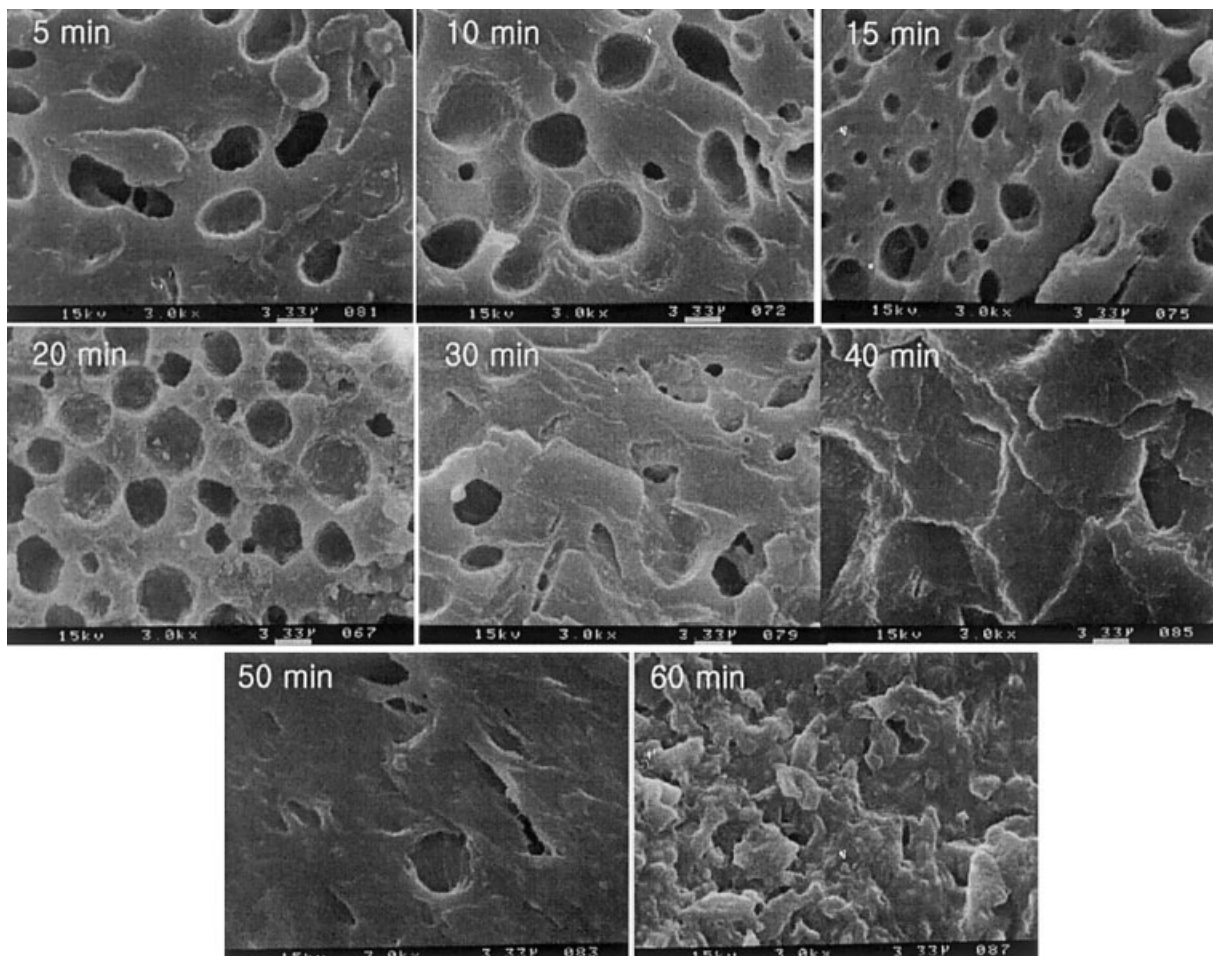
Figure 10 SEM micrographs of THF-etched fracture surfaces of PET/PCL (62.7/37.3 w/w) blends with the blending time.

pared by ester-interchange reactions, the morphology is determined by block characteristics. Therefore, the block characteristics would likely affect biodegradability.

The effect of the blending time on the TOC content of PET/PCL blends is shown in Figure 11. The TOC, based on the weight of the sample, sharply increases with the blending time up to about 20 min (line A), and then the rate at which it increases diminishes (line B). The TOC content is replotted against the sequence length in Figure 12. The TOC content increases with decreasing block length. This suggests that the biodegradability of P(ET/CL) copolyesters depends on the overall crystallinity of the copolyesters, which is largely determined by sequence length. The decrease in the crystallinity is expected to increase biodegradability because it makes the chain more accessible and penetration of the copolyester by the lipase easier. The TOC content of the samples sharply increases over the blending time range of 5–20 min; this rate decreases when the blending time exceeds 30 min. For P(ET/CL) copolyesters, the crystallinity of the CL block decreases with the blending time, but the crystallinity of the ET block remains almost constant (see Fig. 7).

Therefore, the biodegradability of the block copolyester is dependent on the block characteristics of the CL unit rather than on those of the ET unit in the initial stage of the ester-interchange reactions during
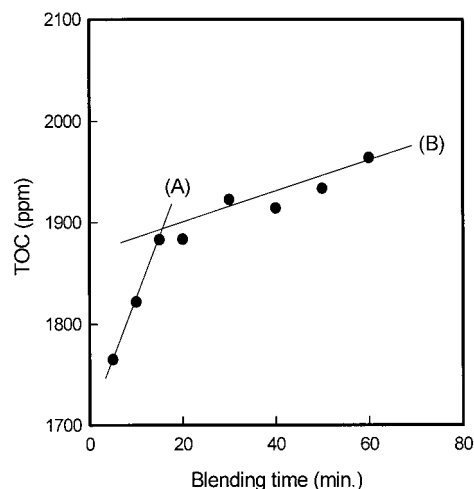
Figure 11 Variation of TOC of PET/PCL (62.7/37.3 w/w) blends with the blending time.
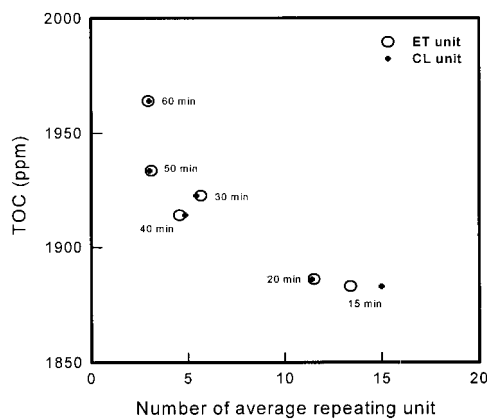
Figure 12 Relationship between the TOC, the blending time, and the number of the average repeating unit of ET and CL blocks in PET/PCL (62.7/37.3 w/w) blends.

melt blending. However, for P(ET/CL) random copolyesters obtained at a blending time of more than 30 min, biodegradability is only dependent on the crystallinity of the ET block because the CL block does not crystallize. Therefore, the crystallinity of the block characteristics is an important factor for the biodegradability of P(ET/CL) copolyesters. These results agree with the fact that an enzyme attack initiates in the amorphous region of a polymer. This suggests that the biodegradation behavior of the P(ET/CL) copolyesters may be regulated by control over the blending time because it can change the block characteristics.

CONCLUSIONS

The block characteristics of P(ET/CL) copolymers can be regulated by control over the blending time in the melt blending of PET and PCL. This is important because the supermolecular structures, such as the crystallinity, which has a decisive effect on the biodegradability of copolyesters, are determined by block characteristics. At a longer blending time, the P(ET/CL) copolymers tend to be random. With a decreasing sequence length for both ET and CL blocks, the melting and crystallization temperatures of P(ET/CL) copolymers decrease. Furthermore, the crystalline structure changes, and the morphology is converted into a homogeneous phase. Therefore, the biodegradability of P(ET/CL) copolyesters increases with a decrease in the sequence length of ET and CL blocks. This suggests that biodegradable copolyesters with desired biodegradability behaviors may be prepared by the melt blending of polymers. This result may be extended to other polyester–polyester melt-blend systems as well.

References

1. Amass, W.; Amass, A.; Tighe, B. Polym Int 1998, 47, 89.
2. Kasuya, K. I.; Takagi, K. I.; Ishiwatari, S. I.; Yoshida, Y.; Doi, Y. Polym Degrad Stab 1998, 59, 327–332.
3. Swift, G. Acc Chem Res 1993, 26, 105–110.
4. Zhu, J.; Shao, T.; Sui, W.; Zhang, S.; Xiao, H.; Tao, X. In Polymers and Biomaterials; Feng, H.; Han, Y.; Huang, L., Eds.; North Holland: New York, 1991; p 387.
5. Domb, J.; Amselem, S.; Maniar, M. In Polymeric Biomaterials; Dumitriu, S., Ed.; Marcel Dekker: New York, 1998; p 399.
6. Zhu, J.; Shao, Y.; Sui, W.; Zhang, S.; Xiao, H.; Tao, X. In Polymers and Biomaterials; Feng, H.; An, Y.; Huang, L., Eds.; Elsevier Science: Amsterdam, 1991; p 387.
7. Benicewicz, B. C.; Shalaby, S. W.; Clemow, A. J. T.; Oser, Z. In Agricultural and Synthetic Polymers; Glass, J. E.; Swift, G., Eds.; American Chemical Society: Washington, DC, 1989; p 161.
8. Robert, T. C.; Michael, Y. J.; John, M. P.; Antonios, G. M. In Biomaterials for Drug and Cell Delivery; Mikos, A. G.; Murphy, M.; Bernstein, H.; Peppas, N. A., Eds.; Materials Research Society: Pennsylvania, 1994; p 33.
9. Yoo, H. Y.; Umemoto, S.; Kikutani, T.; Oki, N. Polymer 1994, 35, 117.
10. Lenz, R. W.; Schuler, A. N. J Polym Sci Polym Symp 1978, 63, 343.
11. Lee, S. C.; Yoon, K. H.; Kim, J. H. Polym J 1997, 79, 1.
12. Backson, S. C. E.; Kenwright, A. M.; Richards, R. W. Polymer 1995, 36, 1991.
13. Lu, X.; Windle, A. H. Polymer 1995, 36, 451.
14. Yoo, E. S.; Yoo, Y.; Im, S. S. J Environ Polym Degrad 1999, 7, 19.
15. Yoo, E. S.; Im, S. S. J Environ Polym Degrad 1998, 6, 223.
16. Huang, S. J. In Comprehensive Polymer Science; Eastmond, G. C.; Ledwith, A.; Russo, S.; Sigwalt, P., Eds.; Pergamon: New York, 1989; Vol. 6, p 597.
17. Tokiwa, Y.; Suzuki, T. J Appl Polym Sci 1981, 26, 441.
18. Tokiwa, Y.; Ando, T.; Suzuki, T.; Takeda, T. Polym Mater Sci Eng 1990, 62, 988.
19. Iwamoto, A.; Tokiwa, Y. Polym Degrad Stab 1994, 45, 205.
20. Kricheldorf, H. R.; Berl, M.; Scharnagl, N. Macromolecules 1988, 21, 286.
21. Trollsas, M.; Atthoff, B.; Claesson, H.; Hedrick, J. L. Macromolecules 1998, 31, 3439.
22. Ma, D.; Zhang, G.; Huang, Z.; Luo, X. J Polym Sci Part A: Polym Chem 1998, 36, 2961.
23. Tang, W.; Murthy, N. S.; Mares, F.; Mcdonnell, M. E.; Curran, S. A. J Appl Polym Sci 1999, 74, 1858.
24. Kotliar, A. M. J Polym Sci Part D: Macromol Rev 1981, 16, 367.
25. Pilati, F.; Marianucci, E.; Berti, C. J Appl Polym Sci 1985, 30, 1267.
26. Kint, D.; Guerra, S. M. Polym Int 1999, 48, 346.
27. Collins, S.; Kenwright, A. M.; Pawson, C.; Peace, S. K.; Richards, R. W. Macromolecules 2000, 33, 2974.
28. Kenwright, A. M.; Peace, S. K.; Richards, R. W.; Bunn, A.; Macdonald, W. A. Polymer 1999, 40, 2035.
29. Kenwright, A. M.; Peace, S. K.; Richards, R. W.; Bunn, A.; Macdonald, W. A. Polymer 1999, 40, 5851.
30. Lee, S. C.; Yoon, K. H.; Park, I. H. Polymer 1997, 38, 4831.
31. Stewart, M. E.; Cox, A. J.; Naylor, D. M. Polymer 1993, 34, 4060.
32. Yoshie, N.; Inoue, Y.; Yoo, H. Y.; Okui, N. Polymer 1992, 31, 1360.
33. Wunderlich, B. Macromolecular Physics; Academic: New York, 1980; Vol. 3, p 261.