Synthesis and Characteristics of Biodegradable Copolyesters from the Transesterification of Poly(butylene adipate-*co*-succinate) and Poly(ethylene terephthalate)

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ABSTRACT: Poly(butylene adipate-*co*-succinate) (PBAS), an aliphatic polyester, is known for its excellent biodegradability, but its physical and mechanical properties are poor. To improve the physical properties, stiff aromatic rings were added to PBAS through transesterification with poly(ethylene terephthalate) (PET). New biodegradable copolyesters were prepared by the intermolecular ester-exchange reactions between molten PBAS and PET. The transesterification reaction was carried out at 280°C without a catalyst. The newly synthesized copolyesters were characterized with ^{1}H-NMR spectroscopy, differential scanning calorimetry, and thermogravimetric analysis. The mechanical properties were measured with a universal test machine, and the biodegrad-ability was also investigated. By the new peaks appearing in ^{1}H-NMR spectra of the copolyesters, the occurrence of the transesterification reaction between PBAS and PET was confirmed. A reduction of the melting temperature was observed for the copolyesters. The elongations at break of the new copolyesters increased for all compositions and reaction times, in comparison with PBAS. However, the tensile strength decreased with the induction of terephthalate units in the copolyesters. The biodegradability of the copolyesters also depended on the number of terephthalate units. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3266–3274, 2004

Key words: polyesters; biodegradable; esterification

INTRODUCTION

Synthetic polymeric materials have been used in whole fields of industrial applications because of their characteristic properties, including low cost, ease of processing, and high ratios of mechanical strength to density. The increase in the usage of polymeric materials reaches over one hundred million tons annually.[1]

Because most polymeric materials have been developed for improved mechanical properties and durability, they preserve the original shapes and properties even after the end of their service life. Plastic waste is regarded as one of the main causes of environmental problems. The solution to these problems involves not only the simple recycling of plastics but also a number of active studies on biodegradable polymeric materials, which can be degraded into small molecules by sunlight, water, or microorganisms in the earth.[2]

It is generally accepted that biodegradable polymers can be degraded by microorganisms if they are under a critical molecular weight. This means that the molecular weight of a biodegradable polymer is an important factor for its biodegradability. There are a few well-known biodegradable polymers, including natural polymers such as starch and cellulose, aliphatic polyurethanes, polyimides, and polyesters,[3] but aliphatic polyurethanes and polyimides show poor biodegradability, despite their high mechanical properties.[4–6]

The aliphatic polyesters, prepared through the step-growth polycondensation of secondary aliphatic alcohols and dibasic aliphatic acids by Carothers in the early 1930s, were brittle and had poor mechanical properties because of their low molecular weight (ca. 5000).[7,8] Showa Highpolymer Co. (Japan) commercialized a high-molecular-weight aliphatic polyester, Bionolle, that was prepared with new catalysts and chain extenders. Bionolle showed improved mechanical properties and had biodegradability similar to that of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate (PHBV) and cellulose.[9–12] However, general aliphatic polyesters had relatively low mechanical properties and melting temperatures (T_m's). A series of studies were undertaken to increase the mechanical properties of aliphatic polyesters through the addition of aromatic units to the polymer main chain.[13–17] Tokiwa and Suzuki[13] tried to embed aromatic units by transesterification, whereas Witt and Muller[15] tried to do the same by the polycondensation of aliphatic and aromatic monomers. Kim et al.[14] also added aromatic units by transesterification between poly(butylene succinate) (PBS) and poly(butylene terephthalate), and
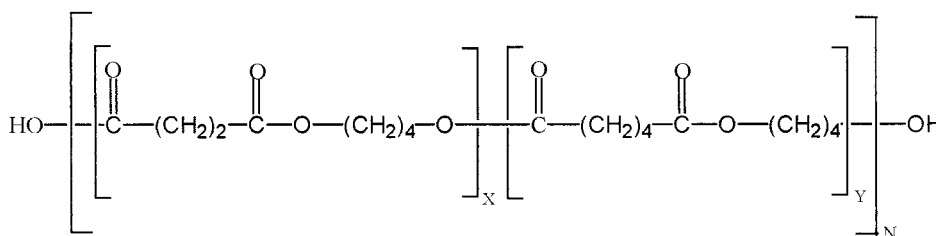
Scheme 1 Chemical structure of PBAS.

they reported that embedded aromatic units enhanced the toughness and thermal stability. BASF has commercialized a new biodegradable polyester, Ecoflex, which consists of several polyester units, containing 1,4-butanediol, dicarbonic acids (e.g., adipic acid), and terephthalic acid.[17]

In this study, we prepared biodegradable polyesters through the transesterification of poly(ethylene terephthalate) (PET) and poly(butylene adipate-co-succinate) (PBAS); 1,4-butanediol, adipic acid, and succinic acid were used as monomers. The transesterification reaction was performed without catalysts. The reaction time and the proportions of PET and PBAS were varied. The thermal and mechanical properties of the new copolyesters were investigated, and the biodegradability of the new copolyesters was also studied.

EXPERIMENTAL

Transesterification

The polyesters used in this study were PBAS (Skygreen SG 2190E) and PET (SKYPET BB-7755) from SK Chemical Co. (Korea). The chemical structure of PBAS is shown in Scheme 1.

PBAS and PET were dry-mixed in weight ratios of 90:10, 80:20, 70:30, 60:40, and 50:50, and 60 g of the mixed polyesters was placed in a reactor equipped with a mechanical stirrer. Argon gas was substituted into the reactor, and this was followed by vacuum degassing. This was repeated five times at 80°C. Mixed polyesters were dried for another 1 h *in vacuo* in the reactor. The reactor was put into an oil bath at 280°C, and the mixed polyesters were melted for 5 min

and then stirred at 60 rpm. The transesterification reaction was performed for 30, 45, 60, 75, and 90 min.

Solution blends

PBAS and PET were dissolved in a mixed solvent of phenol (60 vol %) and 1,1,2,2-tetrachloroethane (40 vol %) at room temperature for 1 h. The solution was poured into methanol, and the precipitated polyesters were dried in a vacuum oven.

Characterization

A Bruker Avance Digital 400 ^{1}H-HMR (400 MHz) spectrometer (Rheinstetten, Germany) was used to confirm the formation of new chemical bonds. As a solvent, deuterated trifluoroacetic acid was used for PET, whereas deuterated chloroform was used for PBAS and the copolyesters.

The T_m and crystallization temperature (T_c) values of the copolyesters were measured with a Seiko DSC 220C differential scanning calorimetry (DSC) instrument calibrated with pure indium as a standard (Japan). To eliminate the thermal history, samples (2.5 ± 0.5 mg) were heated to 280°C at a heating rate of 20°C/min and held there at 280°C for 1 min. T_c was measured while the samples were cooled to −50°C at a rate of 20°C/min, and during the third run, T_m was measured at a heating rate of 20°C/min.

A Seiko TG/DMA320 was used to evaluate the thermal degradation temperature. Samples (5 ± 1 mg) were heated to 600°C at a heating rate of 30°C/min in nitrogen gas.

TABLE I.
Notation of transesterification and solution-blend product

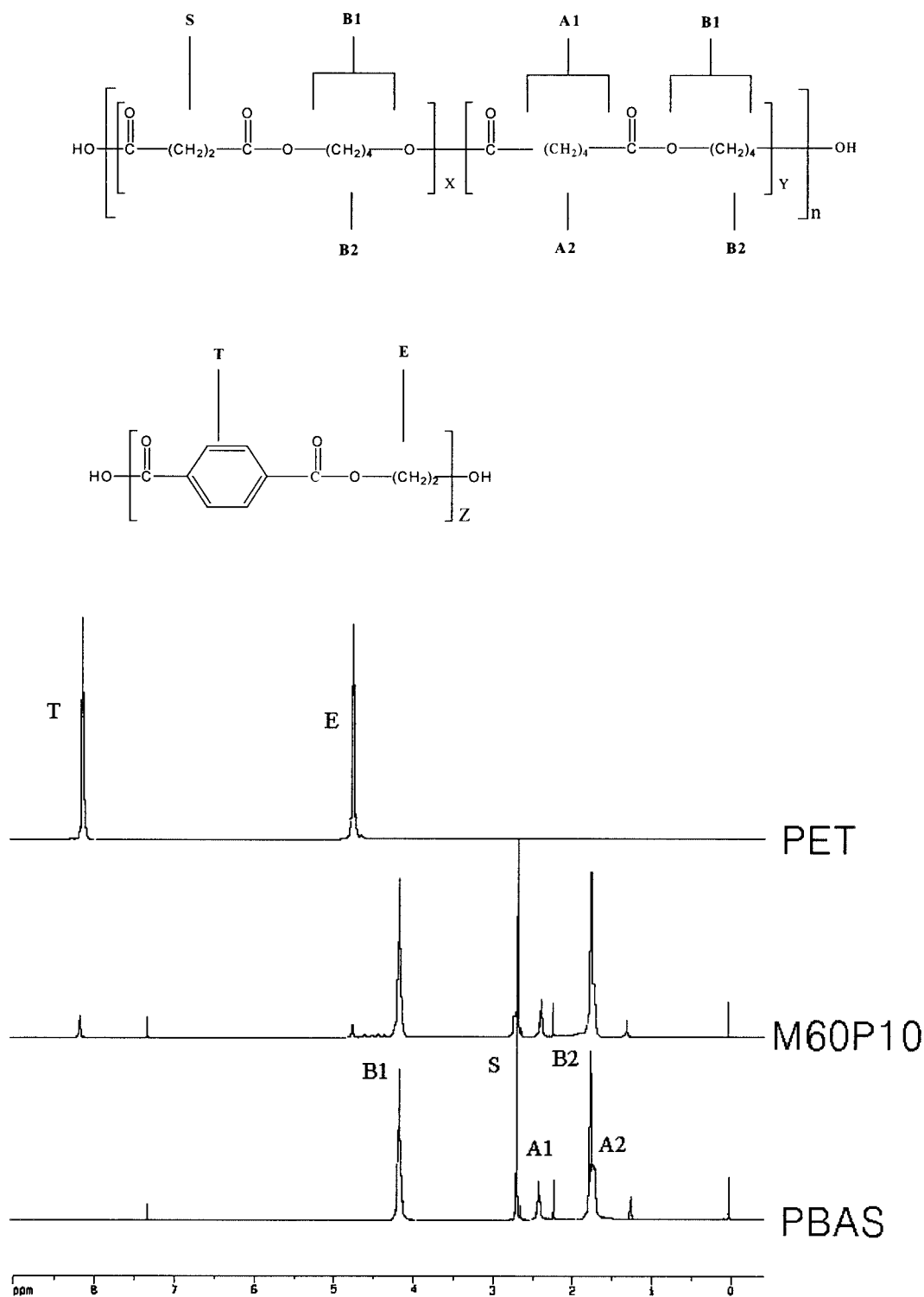| Reaction time (min)	30	45	60	75	90
PET/PBAS = 10/90	M30P10	M45P10	M60P10	M75P10	M90P10
PET/PBAS = 20/80			M60P20		
PET/PBAS = 30/70			M60P30		
PET/PBAS = 40/60			M60P40		
PET/PBAS = 50/50			M60P50		
Solution-blend product (PET/PBAS = 10/90)			SBP10		

Figure 1 ^{1}H-NMR spectra of PET, PBAS, and M60P10.

The tensile strength, modulus, and elongation at break were measured with an Instron model 4465 universal test machine (USA) in accordance with ASTM D 638. Dumbbell-type specimens were used at a crosshead speed of 500 mm/min.

The biodegradability of the copolyesters was investigated through a comparison of the weight loss during the immersion of samples in river water. The samples were put into the river water in polyethylene bottles, and they were held at 37°C for 40 days. The samples were taken out every 10 days and washed with methanol; this was followed by drying in a vacuum oven. The weight losses of the samples were measured, and the surfaces of the
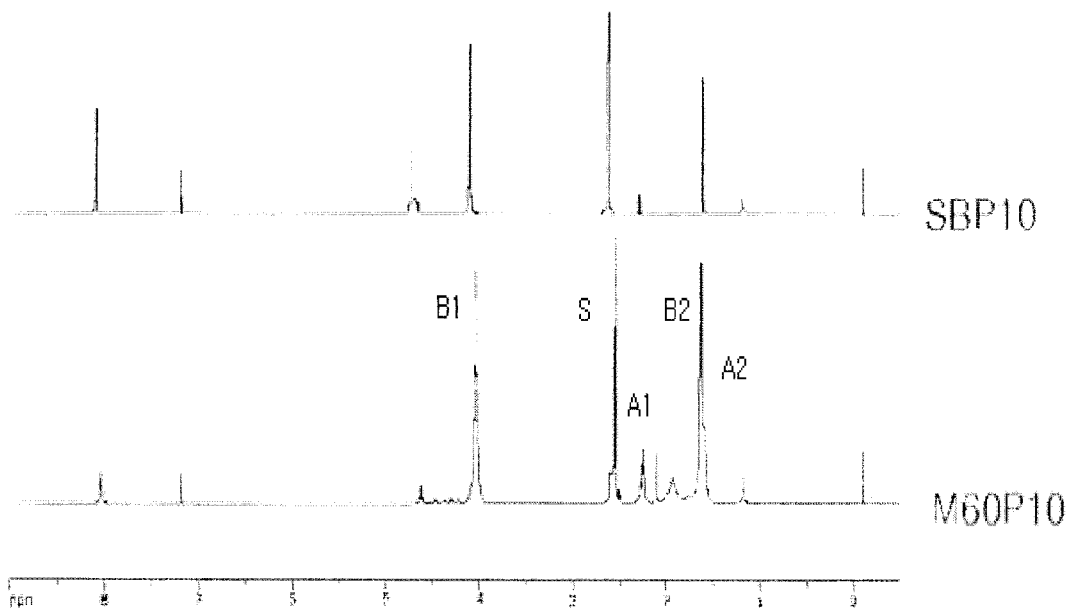
Figure 2 ^{1}H-NMR spectra of M60P10 and a solution blend of PBAS (90 wt %) and PET (10 wt %).

biodegraded samples were observed with a Zeiss Axiolab Pol 0.5 polarized microscope (Germany) at a magnification of 500×.

RESULTS AND DISCUSSION

Analysis

NMR spectra of PBAS, PET, and M60P10 (see Table I for the notation), obtained from the transesterification reaction of 10 wt % PET and 90 wt % PBAS for 10 min, are shown in Figure 1. New characteristic peaks appeared between 4.7 and 4.0 ppm, which were not found for the homopolymers.

In Figure 2, NMR spectra of M60P10 and SBP10, which was from a solution blend of the same ratio of PET and PBAS used for M60P10, are depicted.

On the basis of these results, the existence of new aromatic heterolinkages inside the backbone of the
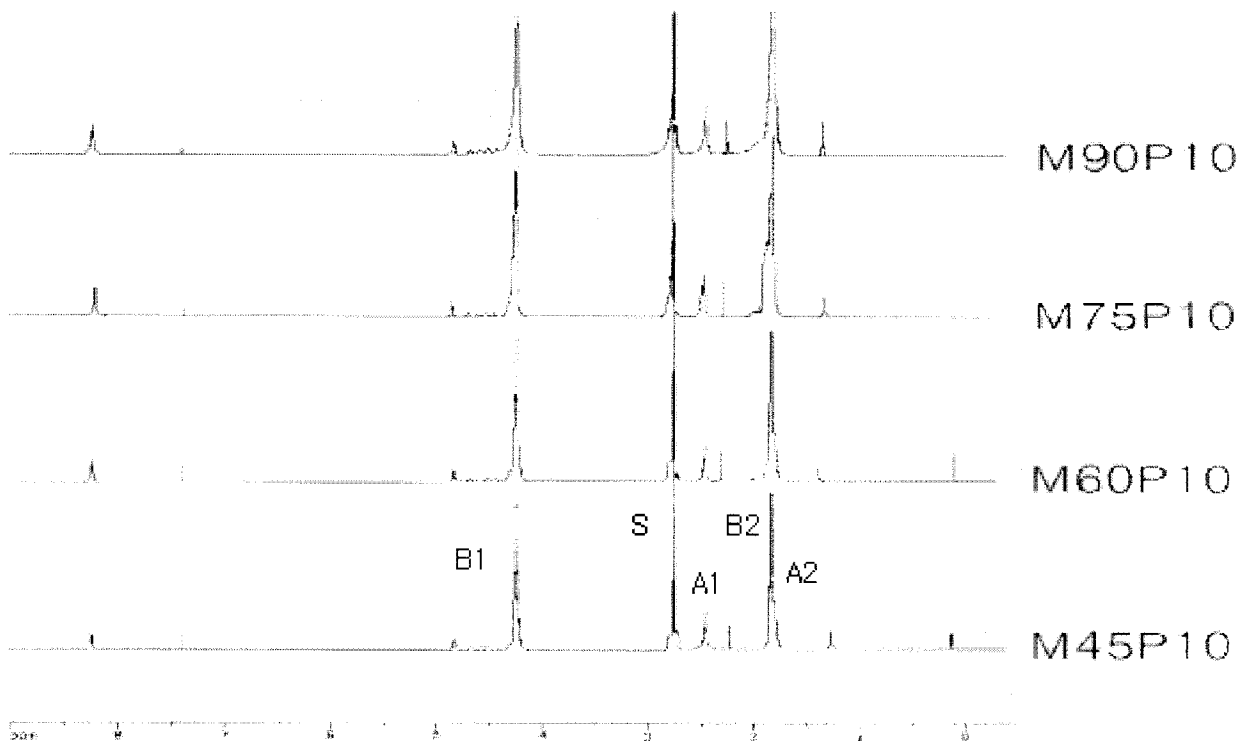
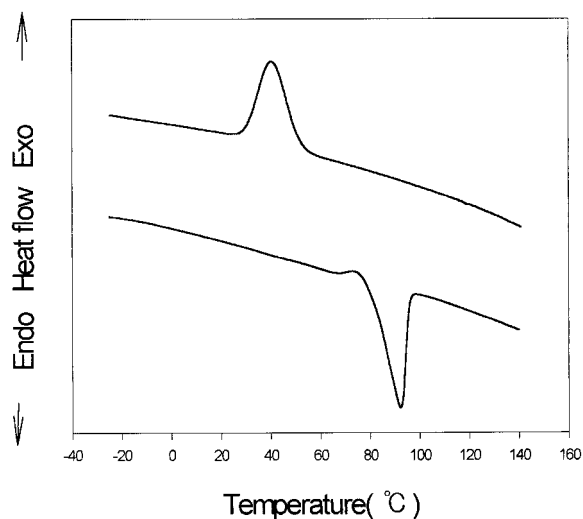**Figure 3** ^{1}H-NMR spectra of the copolyesters with respect to the reaction time.

Figure 4 DSC thermograms of PBAS.

copolyester was confirmed as a result of the transesterification reaction.[16]

The NMR spectra of the copolyesters with respect to the reaction time are shown in Figure 3. The area of the peak from the heterolinkage increased as the reaction time increased, and this means that the content of the aromatic units in the copolyester increased.[16]

Thermal properties

DSC thermograms of PBAS and a solution blend of PBAS and PET are shown in Figures 4 and 5, respectively. T_m of PBAS was about 90°C. As shown in Figure 5, the discrete T_m and T_c peaks from the original PBAS and PET were found. This means that
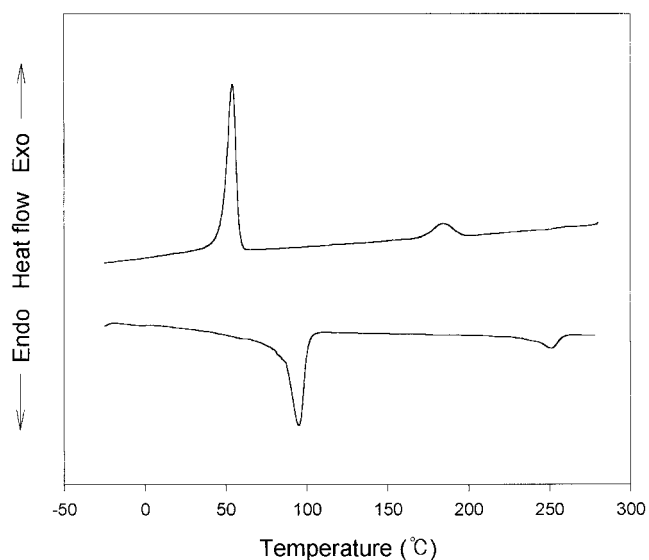

Figure 6 DSC thermograms of the copolyesters with respect to the reaction time.

Figure 5 DSC thermograms of solution blends of PBAS (90 wt %) and PET (10 wt %).
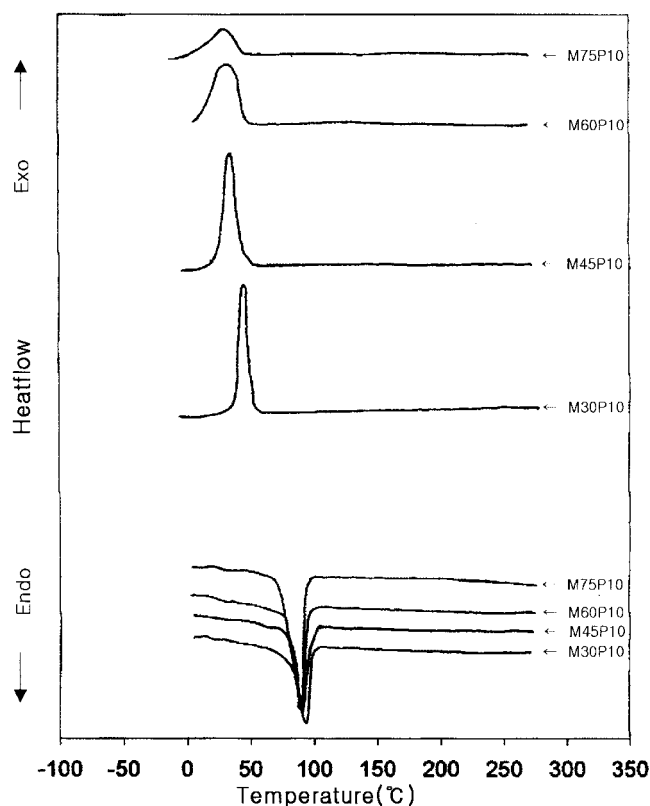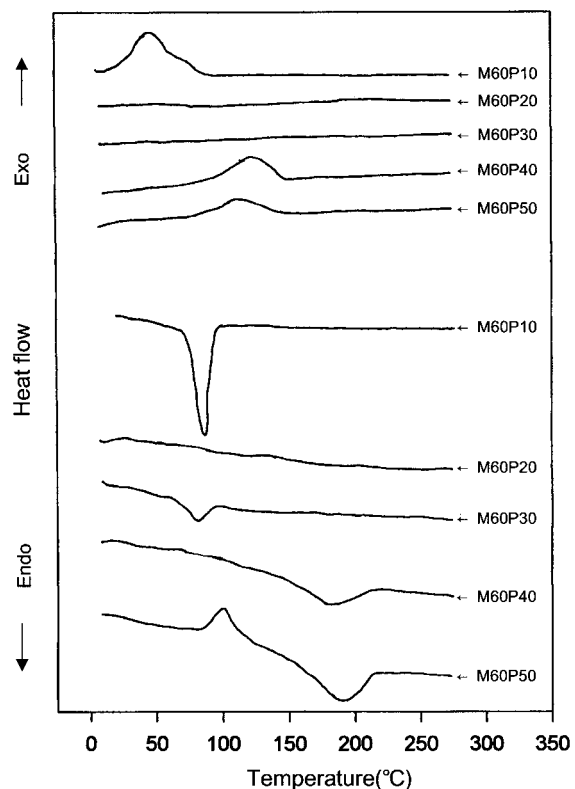

Figure 7 DSC thermograms of the copolyesters with respect to the PET contents.
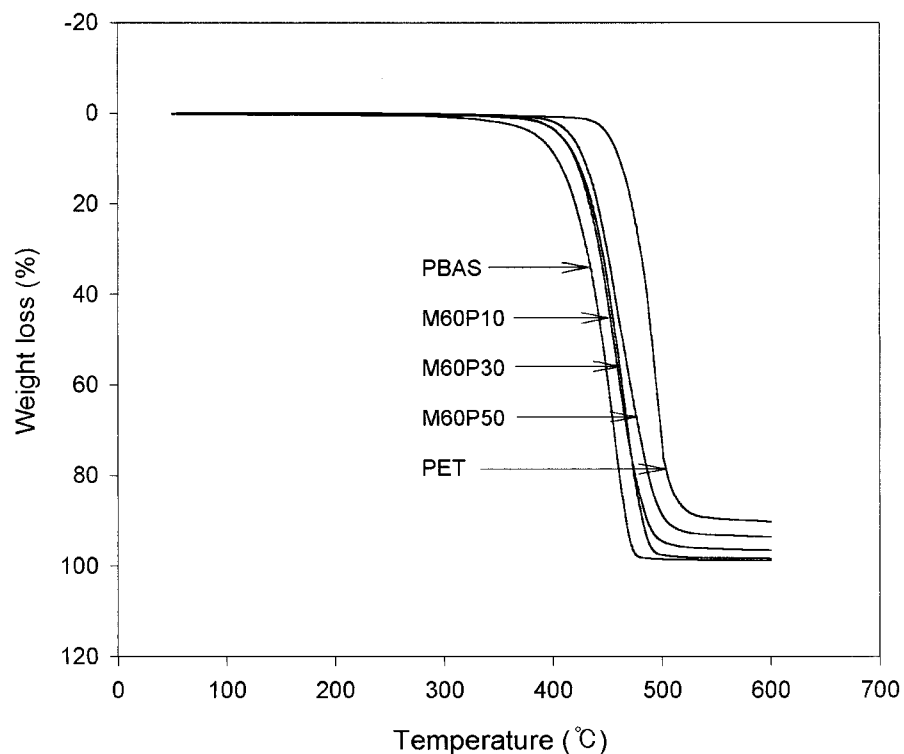
Figure 8 TGA thermograms of PBAS, PET, and the copolyesters.

there was no reaction or no strong molecular interaction between the two compositions in the solution blend.

In Figure 6, DSC thermograms of the copolyesters with 10 wt % PET are shown with respect to the reaction time. The T_m peaks of PET vanished, and
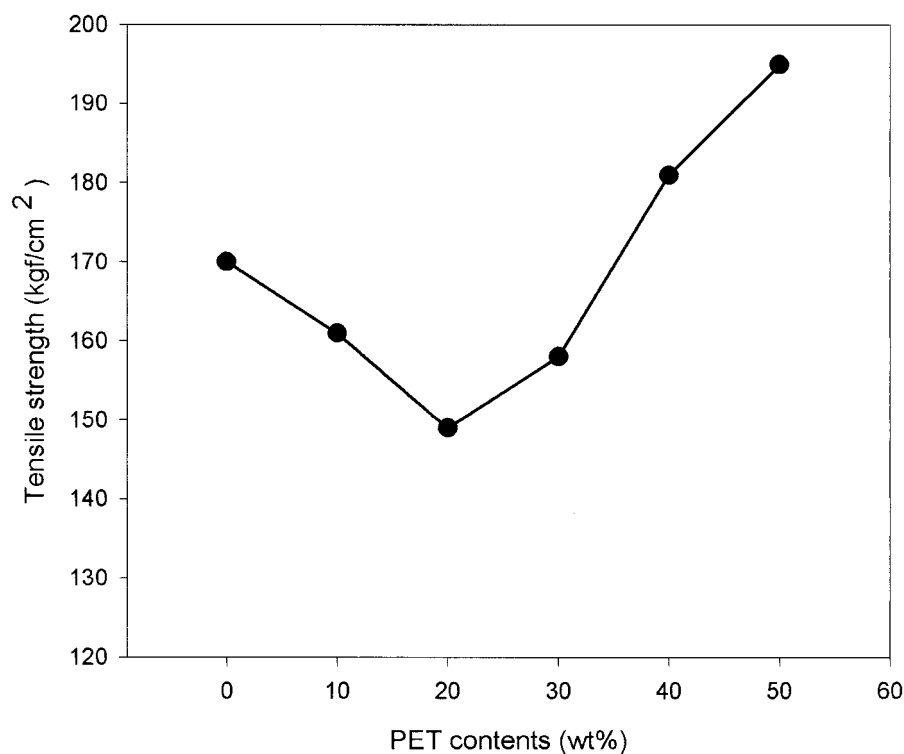

Figure 9 Tensile strength of the copolyesters after a reaction time of 60 min with respect to the PET contents.
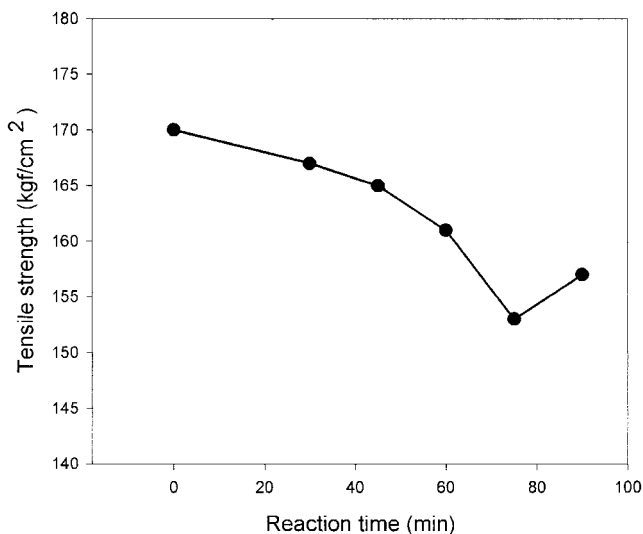
Figure 10 Tensile strength of the copolyesters with 10 wt % PET at various reaction times.
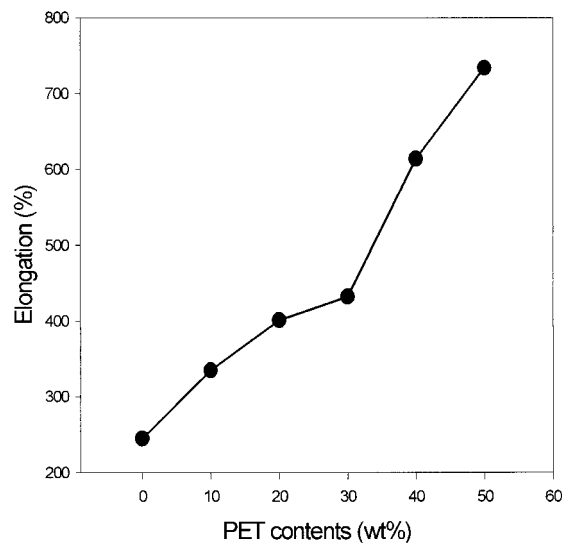

Figure 12 Elongation at break of the copolyesters after a reaction time of 60 min with respect to the PET contents.

those of PBAS shifted a little down to a low temperature as the reaction time increased. These changes in the melting behaviors are consistent with other reports of transesterification between two polymers.[14] They were due to the lowered regularity of the copolyester backbone caused by the introduction of the aromatic units into PBAS. As the main-chain structure of the copolyesters became more random and harder to crystallize, T_m of the copolyesters decreased.

The crystallization behavior showed the same trend as the melting behavior. The crystallization peak became broad and shifted down to a lower temperature as the reaction time increased. The crystallization peak was observed not only in the cooling run but also in

the third run. This was thought to be due to the slower crystallization rate of the copolyesters, which resulted from the structures of the copolyesters being more random than those of PBAS. That is, insufficient crystallization of the copolyesters during the cooling run might cause crystallization of the remaining crystallizable portion of the copolyesters in the third heating run.

In Figure 7, DSC thermograms of the copolyesters after 60 min of reaction time are shown with respect to the different ratios of PET. In the case of M60P20, in which 20 wt % PET was used, the crystallization peaks and melting peaks vanished. Otherwise, only a small crystallization peak was observed for 30 wt % PET.
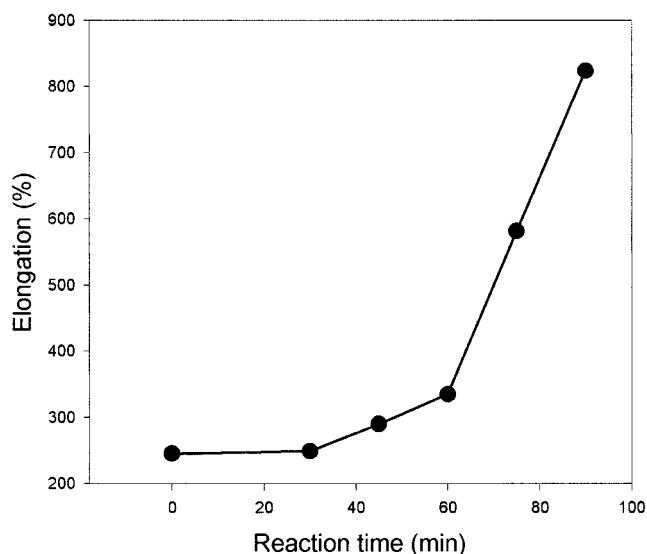

Figure 11 Elongation at break of the copolyesters with 10 wt % PET at various reaction times.
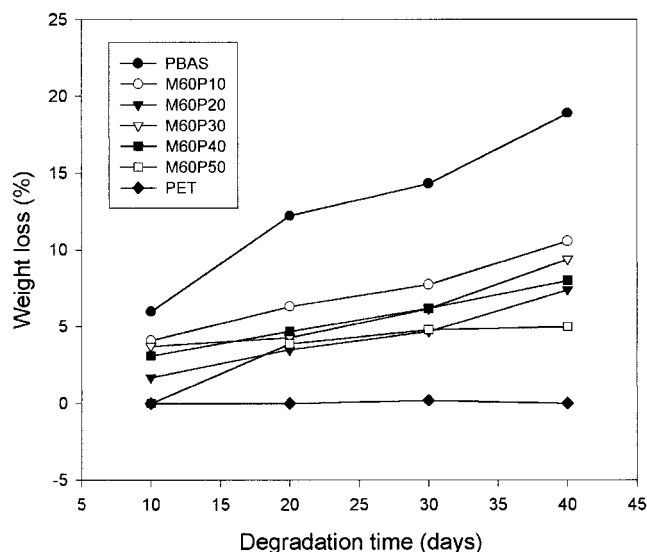

Figure 13 Weight losses of PBAS, PET, and the copolyesters after immersion testing.
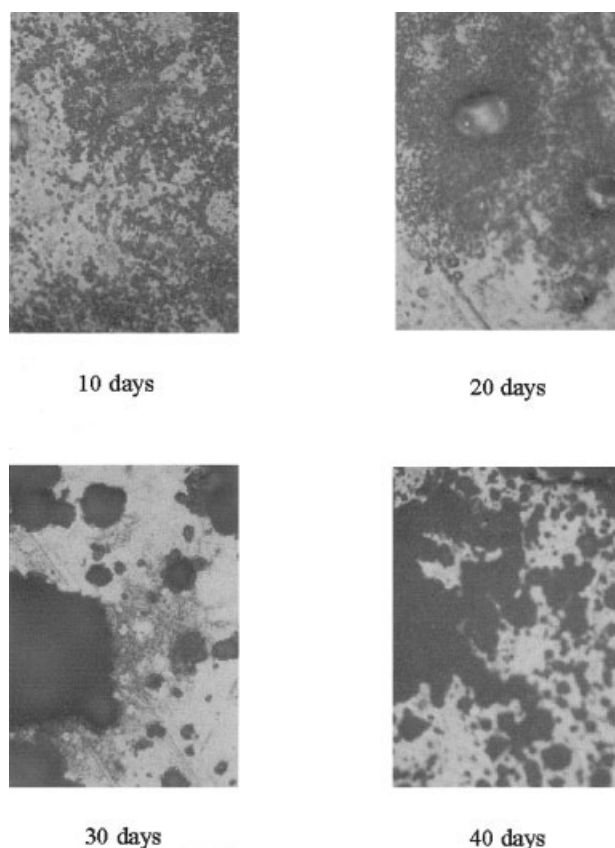
Figure 14 Photographs of PBAS films after degradation testing (original magnification = 500×).

As the PET contents increased beyond 40 wt %, the crystallization peaks and melting peaks appeared, and these were lower than those of PET. It was thought that these resulted from the increased number of embedded aromatic units in the copolyesters and the existence of the longer block of the PET unit.

Figure 8 shows thermogravimetric analysis (TGA) thermograms of the copolyesters with different PET contents. The thermal decomposition temperature rose with the number of PET units. Higher thermal stability was achieved with an increased number of embedded aromatic units, which were thermally more stable than the aliphatic units.

Mechanical properties

The tensile strengths of the copolyesters with various PET contents at a fixed reaction time of 60 min are given in Figure 9, and the tensile strengths of the copolyesters with constant PET contents of 10 wt % with respect to various reaction times are shown in Figure 10.

In comparison with PBAS, the tensile strengths of the copolyesters decreased as the reaction time increased. As the contents of PET increased, the tensile strengths of the copolyesters decreased, but they increased again over 30 wt % PET.

The decrease in the tensile strength with the reaction time was thought to be due to the thermal degradation of the copolyesters, and the increase in the tensile strengths of the copolyesters with PET contents greater than 30 wt % can be explained by the increase in the number of hard PET blocks in the copolyesters.

The elongations at break of the copolyesters with different PET contents are shown in Figure 11. The elongation of PBAS was around 240%, whereas those of the copolyesters increased abruptly up to 800% with the addition of PET.

The effects of various reaction times on the elongation are shown in Figure 12, which shows that the elongation increased as the reaction time increased.

In general, the elongations of the polymer materials were thought to be high when the polymer chain existed in a random-coil conformation without any orientation or crystallization of the chain. The increase in the elongations of the copolyesters was thought to occur because the embedded aromatic units might inhibit the chain orientation or crystallization of the copolyesters.
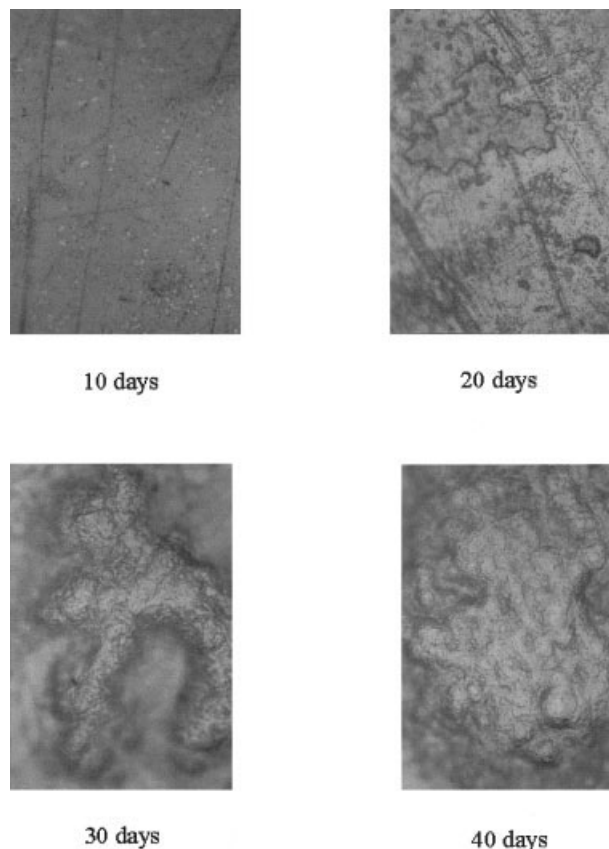

Figure 15 Photographs of M60P10 films after degradation testing (original magnification = 500×).

Biodegradability

The weight losses of PBAS, PET, and the copolyesters after their immersion in river water is illustrated in Figure 13. Biodegradable PBAS showed a 19% weight loss after 40 days, but PET showed no weight changes. The weight losses of the copolyesters were between those of PBAS and PET, depending on their PET contents.

Photographs of PBAS and M60P10 films after immersion tests are shown in Figures 14 and 15, respectively. Dark areas and dents on the surfaces of the samples represented biodegraded parts. The copolyesters produced by transesterification showed good biodegradability.

CONCLUSIONS

In this work, new biodegradable copolyesters were prepared through the transesterification of aliphatic polyesters, PBAS and PET. Their mechanical, thermal, and biodegradable properties were characterized. The existence of new aromatic heterolinkages inside the backbones of the copolyesters, resulting from the transesterification reaction, was confirmed. The T_m and T_c values of the copolyesters varied with the PET contents used for the transesterification reaction. The thermal decomposition temperature increased as the number of embedded aromatic units of PET increased.

The elongations of the copolyesters increased quite a bit with the introduction of aromatic units. However, the tensile strengths of the copolyesters decreased with less than 30 wt % PET and increased with higher PET contents. This was thought to be due to the increased number of hard PET blocks in the copolyesters. The copolyesters prepared in this study showed good biodegradability.

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