Properties of Biodegradable Copolyesters of Succinic Acid-1,4-Butanediol/Succinic Acid-1,4-Cyclohexanedimethanol

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ABSTRACT: Although progress has been made in the study of biodegradable polyesters, little attention was given to aliphatic/alicyclic copolyesters. For this reason, we have undertaken systematic studies on the aliphatic/alicyclic copolyesters. As a first step in our research, we have presented the material characteristics (e.g., thermal and mechanical properties) and the biodegradability in different biological environments for a series of the aliphatic/alicyclic copolyesters that were synthesized by polycondensation of succinic acid, 1,4-butanediol, and 1,4-cyclohexanedimethanol. The chemical composition of the aliphatic/alicyclic copolyesters plays an important role in controlling the material characteristics and biodegradability. For the copolyesters with a mole fraction of succinic acid-1,4-cyclohexanedimethanol <0.3, an adjustment of the optimum between physical properties and biodegradability seems to be feasible. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 553–561, 1999

Key words: aliphatic/alicyclic copolyester; 1,4-cyclohexanedimethanol; biodegradability

INTRODUCTION

The amount of municipal and industrial waste has markedly increased throughout the world in the last few years. Waste disposal is becoming a serious environmental problem, because of limited landfill capacity and incineration facilities. Environmental concerns have caused scientists to accelerate their activities in the design and study of materials that are constructed to degrade to safe components in a desirable frame under specified environmental conditions.

A number of biodegradable polyesters have been developed up to now and some of them are

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commercially available (e.g., PHB, PCL, Bionolle). All of these polyesters are based exclusively on aliphatic monomers. Although these aliphatic polyesters can proceed to commercial products applicable for various purposes, they exhibit some disadvantages. Material characteristics are sometimes not suitable for distinct applications (e.g., melting point of PCL: $\sim 60^{\circ}$ C) or can be adapted only in a limited extent to specific product requirements. In some cases, the price is the factor excluding the materials from widespread commercialization. In contrast, pure aromatic polyesters, like poly(ethylene terephthalate) (PET), which are produced in large scale, display satisfactory properties, but are resistant to a microbial attack.

Recently, Witt and colleagues¹ reported that aliphatic/aromatic copolyesters in a defined window of monomer composition and with a specific monomer distribution in the polymer chains com-

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bine good material properties, a reasonable price level, and biodegradability. Especially copolyesters from 1,4-butanediol (BD), adipic acid, and terephthalic acid turned out to be very interesting with regard to a commercial application as biodegradable materials in packing and other applications. Tokiwa and Suzuki^{2,3} indicated that the physical properties of aliphatic polyesters are improved by adding aromatic polyester to the polymer chains. They also suggested that the biodegradation rate of copolyesters made from aliphatic and aromatic polyesters can be regulated by controlling the reaction time of transesterification or composition. However, there seems to be an ongoing debate concerning whether aromatic oligomers through cleavage of ester bonds by enzymatically or chemically catalyzed hydrolysis are completely biodegradable.

Although progress has been made in the study of biodegradable polyesters, little attention was given to aliphatic/alicyclic copolyesters. There is apparently little literature data concerning material characteristics and biodegradability of aliphatic/alicyclic copolyesters. For this reason, we have decided to undertake systematic studies on the aliphatic/alicyclic copolyesters. As a first step of our research, we presented the synthesis, the material characteristics, and the biodegradability in different biological environments for a new group of biodegradable copolyesters.

EXPERIMENTAL

Polymer Preparation

Aliphatic/alicyclic copolyesters were synthesized by conventional polycondensation techniques. In a typical polymerization, succinic acid (SA) was reacted with 1.5 mole BD/mol of SA in the presence of tetraisopropyl titanate (30 ppm in term of T_i metal) at 200–205°C in a nitrogen atmosphere. SA also reacted with 1.5 mol of 1,4-cyclohexanedimethanol (CHDM)/mol of SA. After the esterification reaction, copolymerization was conducted with two reaction products (butylene succinate SA-BD and cyclohexanedimethylene succinate SA-CHDM oligomers) at 220°C under reduced pressure of 0.5-0.6 Torr for 5-8 h. During this stage, the torque measured increased slowly until a constant value was reached. The composition of the copolyesters investigated is given in Table I.

Table I Composition of Copolyesters of SA-BD/SA-CHDM

Sample Code	Mol Ratio of SA-BD/SA-CHDM			
P10	90/10			
P20	80/20			
P30	70/30			
P40	60/40			

Characterization

The molecular weights of the copolyesters were estimated from intrinsic viscosity measurement and gel permeation chromatography. Viscometic measurements were conducted with a solution of 0.050 g of polymer in 10 mL of chloroform, using an Ubbelohde viscometer thermostated at 25°C. Gel permeation chromatography measurements were conducted on a Waters 150-CV equipped with a differential refractometer for detection. Polystyrene standards with a low polymer dispersity were used to make a calibration curve. For most of the polymer characterizations, the 3-mmthick injection-molded bars were remelted at 135°C and compression-molded into thinner (0.5 mm thick) sheets, which were slowly cooled to room temperature in the air. Thermal analysis was performed using a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) and a Polymer Laboratories dynamic mechanical thermal analyzer Mk III. The dynamic mechanical thermal analyzer was operated in the dual cantilevers bending mode at a frequence of 1 Hz and a heating rate of 3°C min⁻¹ over the temperature range of -100 to 50°C. Wide angle X-ray diffractions were measured using a JEOL JDX-11 P3A X-ray diffractometer with Ni-filtered CuK_{\alpha} radiation. X-ray crystallinity was determined by the area ratio of the crystalline peaks and the amorphous halo. The morphology of spherulites was examined using a Nikon polarizing optical microscope equipped with a Mettler hot stage. Tensile tests were performed with an Instron Model 4201 universal testing machine using a gauge length of 30 mm and a crosshead speed of 250 mm min⁻¹. Data were taken as averages of at least five measurements.

Biodegradation Test

The biodegradation test was done by liquid culture experiments along the general lines of ASTM D5209-91. The test method consists of selecting

microorganisms for the determination of aerobic biodegradability, preparing inoculum, exposing samples to the activated inoculum, measuring CO₂ evolved as a function of time, and assessing the degree of biodegradability. The apparatus was divided into three parts: the unit which removed CO₂ from the air, the culture unit, and the CO₂ collector. CO₂ was produced as a result of metabolism of the carbon atoms in the polymer molecules by microorganisms in the aerobic condition. CO₂, thus produced, was collected by Ba(OH)₂ and titrated by HCl. The specimen was cultured at 25 ± 1 °C in the test bottle containing 100 mL of the test medium and microorganisms. In this work, activated sludge was used for the biodegradation test. The activated sludge was harvested from Nanjido Municipal Sewage Treatment Plant in Seoul. Bioassimilable organic substances in the activated sludge were exhausted after 24 h of aeration. The resulting solution was allowed to settle, and the supernatant was collected and stored at 4°C for inoculation. Viable cell number as inoculum was kept at 1×10^6 –1 $imes 10^7 \, cell \, mL^{-1}$. All the biodegradation data were reported as the % carbon converted to CO₂ based on original carbon content. To be more accurate, this test was conducted four times simultaneously and all data were averaged. From the average of four tests, the deviation value was <10%. In addition, simple soil degradation tests were conducted. Soil was obtained from an agricultural field in the Inchon area and used as an incubation medium. The soil was placed in PVC containers. The film samples were laid down between two layers of soil maintained soft to promote the metabolic activity through a proper oxygen uptake. The containers were left in an incubator at 28°C and at a humidity of \sim 70%. The degraded samples were taken every week, and the changes in appearance were observed.

RESULTS AND DISCUSSION

Characterization of Copolyesters

The dependence of melting temperature on the amount of SA-CHDM in the copolyesters is shown in Figure 1. The melting temperature is very sensitive to the amount of the comonomer units SA-CHDM as expected in random copolymers. The melting temperature decreases by $\sim 65^{\circ}\mathrm{C}$ when the SA-CHDM content rises to 40.0 mol %.

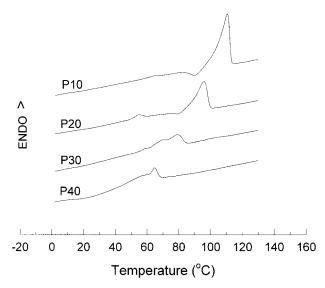


Figure 1 DSC melting thermograms of the copolyesters obtained at a scan rate of 10.0°C min⁻¹.

The problem with structure and properties of copolymers and, more specifically, the relation between melting behavior and composition is not yet satisfactorily solved. One of the most important questions is that of the distribution of comonomer units in the crystalline and noncrystalline regions of a semicrystalline copolymer consisting of A and B units. There are two basic models describing this situation. The first one proposed by Flory⁵ assumes that the comonomeric units, B, are not included in crystallites. They remain in an amorphous phase. According to the second model developed by Eby⁶ and Sanchez and Eby, there is full compatibility between the monomers of both types (i.e., the comonomer B, as well as A build up the crystalline lattice). Analyzing experimental data for different kinds of copolymers, Wegner⁸ compared the two models and concluded that they merely represent two extreme cases. Nevertheless it is possible to establish which of the two models is more applicable for explaining the structure and properties of a given copolymer.

Because of the uncertain determination of the value of surface energy, σ_e , we applied the widely known Flory equation in its classical form:

$$rac{1}{T_m'} - rac{1}{T_m} \, = \, - rac{R}{\Delta H_m} \ln X_{\!A}$$

where T_m is melting temperature of the homopolyester SA-BD, T_m^\prime is melting temperature

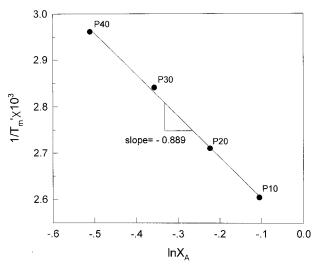


Figure 2 Determination of heat of fusion, ΔH_m using a plot of $1/T_m$ against $\ln X_A$ for the copolyesters.

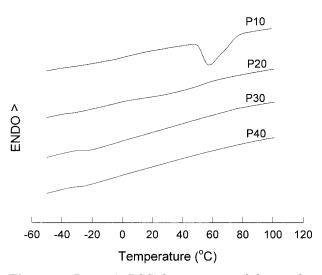


Figure 3 Dynamic DSC thermograms of the copolyesters measured at a cooling rate of 10.0°C min⁻¹.

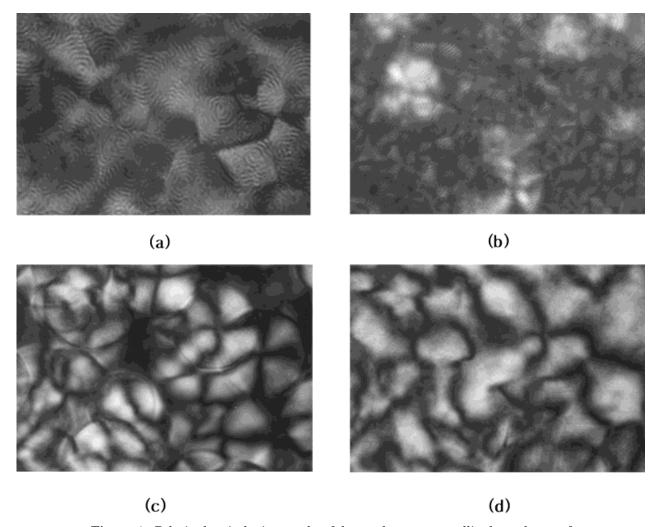


Figure 4 Polarized optical micrographs of the copolyesters crystallized at a degree of supercooling, $\Delta T=30$ °C. (a) P10. (b) P20. (c) P30. (d) P40.

of the copolyesters, ΔH_m is heat of fusion per mole of crystalline mers, and X_A is mole fraction of SA-BD. From the slope of $1/T'_m$ vs. ln X_A plot (Figure 2), ΔH_m can be evaluated. The calculation yields $\Delta H_m = 9.25 \text{ kJ mol}^{-1}$. This value is quite low in comparison with that reported in the literature ($\Delta H_m = 19.0 \text{ kJ mol}^{-1}$). 9,10 This deviation from the theory of Flory indicates that a large portion of noncrystallizable comonomeric units (SA-CHDM) may be trapped in the crystal lattice in the form of crystal defects not excluded from the crystal lattice. It is also pointed out that morphological effect rather than thermodynamic effect should be responsible for the melting behavior of the copolyesters. A kinetic inclusion of defects during crystallization may cause development of metastable crystals, resulting in multiple melting characteristics (as shown in Figure 1).

Figure 3 shows the crystallization behavior studied by dynamic DSC. Samples were heated to 135°C and kept for 5 min to erase previous thermal history, and then crystallized at a constant cooling rate of 10.0°C min⁻¹ in a nitrogen atmosphere. The overall crystallization rate significantly decreases with increasing SA-CHDM content, and a very broad exothermic peak is observed for the samples >20.0 mol % of SA-CHDM in the range of undercooling examined. When a copolymer crystallizes, crystallization rates are influenced by the presence of noncrystallizable components. The noncrystallizable components, such as SA-CHDM units, may retard the rate of transport of crystallizable species, decreasing the rate of crystallization. This effect will be increasingly important as the concentration of noncrystallizable components increases. Another effect that should be taken into account results from the fact that the noncrystallizable units included and/or excluded in the crystal lattice may induce some perturbation on the surface of lamellar crystals by increasing the entropy of folding.¹¹ An increase of surface-free energy, σ_e , due to surface perturbation, causes further depression of the crystallization rate. It is then likely that slow down in the crystallization at a higher concentration of SA-CHDM is ascribed to the combined influence of both the transport term ΔF^* and the thermodynamic term Φ^* , which appear in the Turnbull-Fisher equation. 11

Figure 4 shows polarized optical micrographs of the copolyesters isothermally crystallized at a degree of supercooling, $\Delta T = 30$ °C. In addition to the typical Maltese cross, the concentric banding pattern is observed in the copolyesters with low

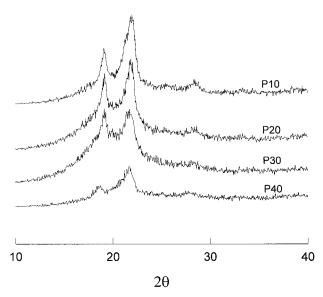


Figure 5 Wide angle X-ray diffraction patterns of compression-molded copolyester samples.

and intermediate SA-CHDM content. This banding implies that the chain axis is periodically rotated around a radial direction. It is believed that the reason for the twisted crystallization, giving rise to the above concentric banding, is stresses set up during crystallization. However, progress in understanding this phenomenon is greatly hindered by lack of detailed knowledge of spherulitic microstructure, and there is no agreement as to what these might be in particular. 12 When concentration of the noncrystallizable components increases in a series of the copolyesters, the perfection (anisotropic ordering) of spherulites decreases and the regular concentric arrangement disappears. Indeed, in the copolyester P40, which contains 40 mol % SA-CHDM, the arms of the Maltese cross are not clearly seen. It should be noted that, although P40 does not display the morphology of well-developed spherulites, it is nevertheless a semicrystalline polymer.

A comparison of the X-ray diffraction patterns of the compression-molded copolyester samples is given in Figure 5. The sharp diffraction peaks are indicative of the presence of crystallites in the copolyesters. The samples of high SA-CHDM contents show relatively weak crystalline peaks that are caused by a reduction in crystallinity and introduction of irregularity. However, there is no essential difference in the X-ray diffraction angles even for the sample of 40 mol % SA-CHDM content. This implies that the aggregation of crystallizable segments and formation of crystalline do-

P20

P30

P40

Sample Code	$\begin{array}{c} [\eta] \\ (dL \ g^{-1}) \end{array}$	$M_n \times 10^{-4}$ (g mol ⁻¹)	M_w/M_n	$T_m \\ (^{\circ}\mathrm{C})$	T_{g} (°C)	X_c
P10	1.568	5.78	2.4	111.0	0.4	33.8

2.1

2.3

2.1

Table II Molecular Weight and Thermal Properties of the Copolyesters

5.34

5.44

5.73

main is not significantly affected by noncrystallizable units. When considering the previous discussion in Figure 2, it also suggests that some SA-CHDM units may be co-crystallized in the SA-BD crystal lattice by a small distortion of the unit cell. The degree of crystallinity, X_c obtained from diffracted intensity data in the range 2θ = 10°-35°C and other characteristics of the copolyesters are listed in Table II. The trend of decreasing the X_c with increasing SA-CHDM content is clearly observed.

1.429

1.238

1.187

The storage modulus E' and the dissipation factor tan δ of the four copolyester samples are plotted in Figure 6 as a function of temperature. In the temperature range from -20°C to -5°C , E'starts to fall due to the onset of amorphous softening near the glass transition. The samples show a single glass transition, the temperature of which shifts to higher temperatures with increasing SA-CHDM content of the copolyesters. The single glass transition temperature, T_{g} suggests that all chain segments in the copolyesters will experience equivalent or average free volumes. 13 The comparative plot shows that the T_{σ} is relatively insensitive to the content of SA-CHDM in the copolyesters. However the tan δ peak is very dependent on the content of SA-CHDM. As the concentration of SA-CHDM increases, the magnitude of the tan δ peak significantly increases. This is consistent with the fact that increasing the concentration of SA-CHDM reduces the overall crystallinity level of the copolyesters, which in-

96.1

79.0

64.7

6.6

10.2

10.8

28.2

19.6

15.8

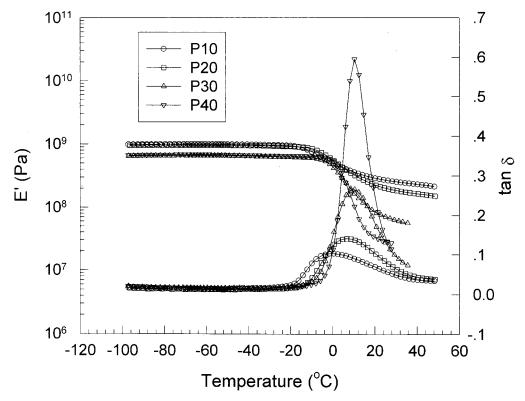


Figure 6 Storage modulus, E', and loss tangent, tan δ , of the copolyesters.

creases their flexibility. It is worth noting that the broadness of tan δ peak conspicuously increases in the P10 copolyester. Miller and colleagues 14 have demonstrated that the broad glass transition does not necessarily imply morphological heterogeneity. Rather, a broad tan δ can be ascribed to the difference in molecular motions of components with nonequivalent free volumes. In semicrystalline polymers, the glass transition arises from purely amorphous chains and amorphous chains which is under restraint due to the vicinity of crystallites. The effect of the hindered chain motion increases with the degree of crystallinity, causing an increase of broadness in the tan δ peaks.

Mechanical Properties

Results of mechanical tests on the copolyester samples are shown in Figure 7. The tensile strength is largely unaffected, whereas the elongation at break remarkably increases with increasing content of SA-CHDM. The sample of 40 mol % SA-CHDM content shows 620% elongation at break. These changes in mechanical properties, of course, reflect the character of SA-CHDM units in the copolyesters. At high SA-CHDM content, where the crystallinity of the copolyesters is suppressed, the tangent modulus of the copolyesters is relatively low. However, the SA-CHDM segments largely contribute to an increase in the elongation at break, leading to good tensile strength of the copolyesters.

Microbial Degradation

Figure 8 shows the biodegradability of the copolyesters investigated by the modified sturm test.

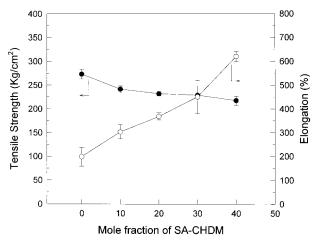


Figure 7 Tensile properties of the copolyesters.

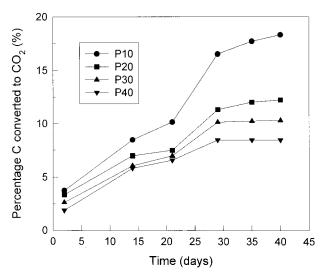


Figure 8 % C converted to CO₂ with time.

The rate of biodegradation decreases with increasing the SA-CHDM content in the copolyesters. The microbial degradation of crystalline aliphatic polyesters proceeds in a selective manner, with the amorphous regions being degraded before degradation of the crystalline region. 15 This suggests that the degree of crystallinity is an important factor in determining the microbial degradability. However, the effect of the degree of crystallinity on the biodegradation rate cannot be observed in this study, because the influence of chemical structure on biological resistance predominates the biodegradability of the copolyesters. In the samples of high SA-CHDM content (e.g., P40), very limited degradation is exhibited during the first 30 days.

Biodegradability tests for 6 weeks in soil are shown in Figure 9. As previously described, the copolyester samples with a molar fraction of SA-CHDM larger than 0.3 show limited degradation in the liquid test media. In contrast, there are significant changes in the appearance of the copolyester films buried in soil. After 4 weeks, the copolyester films became brittle and fragmented very easily, which made it difficult to measure their dimensions. The mass loss accompanied by a considerable mechanical loss indicates that the copolyesters are fairly sensitive to microbial degradation in soil. The relatively large decrease in mechanical properties at the beginning of soil burial tests suggests that random chain scission is the primary mechanism in biodegradation of the copolyesters. The differences in biodegradation observed by application of two different deg-

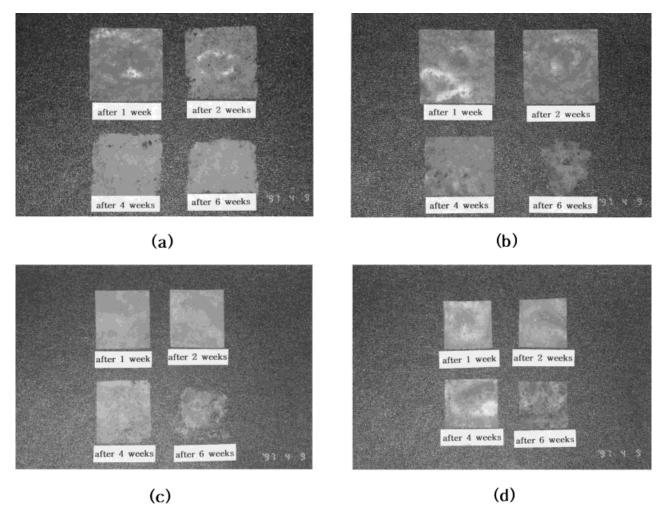


Figure 9 Biodegradation in soil. (a) P10. (b) P20. (c) P30. (d) P40.

radation tests elucidates the necessity to use well-defined laboratory tests for a final judgment of biodegradability. Further investigations will concentrate on the question whether or not only the aliphatic chains in the copolyesters are exclusively biodegraded and what the fate of the alicyclic units is.

CONCLUSIONS

This study has revealed a dependence of material characteristics and biodegradability on the chemical composition of the aliphatic/alicyclic copolyesters. For the copolyesters with a molar fraction of SA-CHDM approximately < 0.3, an adjustment of the optimum between physical properties and biodegradability seems to be feasible. Thus, controlling the biological properties of a plastic ma-

terial by its chemical structure is a promising subject in the final design of biodegradable polymers. The significant differences in biodegradation observed by application of two different degradation tests suggests the necessity to use well-defined test methods for a final judgment of biodegradability.

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