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Synthesis and enzymatic degradation of poly(tetramethylene succinate) copolymers with terephthalic acid

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Abstract

Poly(tetramethylene succinate/terephthalate) copolymers were prepared by melt polycondensation of succinic acid (4) and dimethyl terephthalate (T) with 1,4-butanediol (4G). The structure and physical properties of these copolymers were characterized by ^{1}H NMR, solution viscosity, differential scanning calorimeter and tensile test. The enzymatic degradation was performed in a buffer solution with *Rhizopus delemar* lipase at 37°C. The highest degradation rate was observed for T-17 film due to the depressed crystallinity. T-17 film uniaxially drawn with draw ratio of three times showed the larger tensile strength as well as the much faster degradation rate compared with 4G4 film. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(tetramethylene succinate) copolymer; Terephthalic acid; Enzymatic degradation

1. Introduction

Synthetic aliphatic polyesters such as poly(L-lactic acid), poly(ϵ-caprolactone), and poly(1,4-butanediol succinate) are commercially important biodegradable polymers; however for industrial application their physical properties are often inferior to those of commodity synthetic polymers, which makes hard their use as a material in various fields. The copolymerization of aromatic component with rigid chemical structure into aliphatic polyesters would be expected to improve their thermal and mechanical properties. Some copolyesters containing terephthaloyl unit in the main chain have been prepared by transesterification reaction of poly(ethylene terephthalate) and aliphatic polyesters, and their susceptibilities to lipase enzyme have been studied [1,2]. Witt et al. also have prepared biodegradable copolyesters composed of 1,3-propane diol and adipic acid or sebacic acid with terephthalic acid as comonomer [3,4].

In this study, we have prepared poly(tetramethylene succinate/terephthalate) copolymers to obtain biodegradable polymers with good mechanical and thermal properties. The effect of copolymer composition and drawing on the thermal and mechanical properties as well as enzymatic degradation was investigated.

2. Experimental

2.1. Preparation of copolyesters

Succinic acid (4), dimethyl terephthalate (T) and 1,4-butanediol (4G) were used as received.

Copolymers were prepared by a typical melt polycondensation method. For T comonomer content below 60 mol%, mixture of 10 mmol of succinic acid and dimethyl terephthalate and 11 mmol of 1,4-butanediol with titanium tetraisopropoxide (0.5 wt% of total weight of monomers) as a catalyst was heated at 190–200°C for 2 h in a stream of nitrogen gas, and then heated at 220–230°C for 3 h in a vacuum of 0.1–0.5 torr. For T comonomer content above 70 mol% including poly(tetramethylene terephthalate) homopolymer, mixture of 3 mmol of succinic acid and 7 mmol of dimethyl terephthalate and 50 mmol of 1,4-butanediol with titanium tetraisopropoxide (0.5 wt% of total weight of monomers) and zinc acetate (20 mg) as a catalyst was heated at 190–200°C for 2 h in a stream of nitrogen gas, and then heated at 250–260°C for 3 h, and finally 275–280°C for 1 h in a vacuum of 0.1–0.5 torr. Copolymers are denoted by the contents of terephthaloyl unit. For example, copolymer with the composition of 70 mol% of 4 and 30 mol% of T is denoted as T-30.

The copolymers obtained were melt pressed and subsequently quenched in ice water. These films were dried

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Table 1
Composition of copolymers and η_{SP}/C

Composition in feed (T mol%)	Composition in copolymer (T mol%)[a]	η_{SP}/C (d1/g)[b]
0	0	0.78
10	5	0.63
15	11	0.81
20	17	0.74
30	30	0.83
40	42	0.65
50	52	0.51
70	73	0.55[c]
100	100	0.53[c]

[a] Determined from ^{1}H NMR spectra except for $T = 0$ and $T = 100$.

[b] 0.1 g/10 ml in chloroform at 30°C.

[c] 0.1 g/10 ml in phenol/1,1,2,2-tetrachloethane (60/40 by weight) at 30°C.

overnight at room temperature in vacuo for 24 h and stored in a dry desiccator.

2.2. Characterization

Reduced specific viscosity was measured at 30°C with 1% chloroform solution for T-0–50, and 1% phenol/1,1,2,2-tetrachroloethane (60/40 by weight) solution for T-70 and T-100, respectively. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained at 25°C in deuterated chloroform using a JEOL JNM-EX90A FT-NMR spectrometer with tetramethylsilane as the internal standard. Differential scanning calorimetry (DSC) was carried out on a Perkin–Elmer DSC 7 differential scanning calorimeter with a heating rate of 10°C/min in a nitrogen atmosphere. Tensile test was performed with an Iwamoto tensile tester at a strain of 100%/min to measure tensile strength, elongation and Young's modulus. Average value for 5–10 specimens was employed.

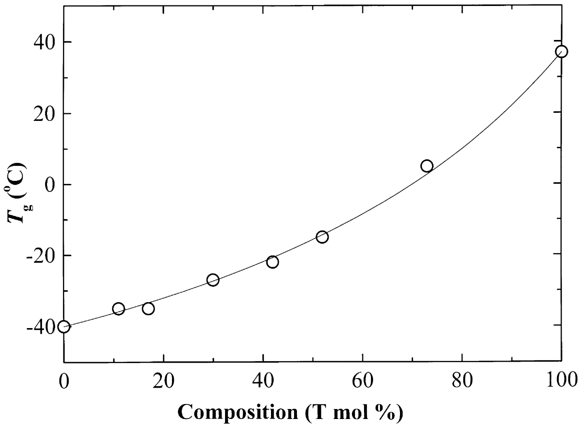

Fig. 1. Plot of T_g values of copolymers measured by DSC versus copolymer composition. The curve is that predicted by the Wood's equation [5].

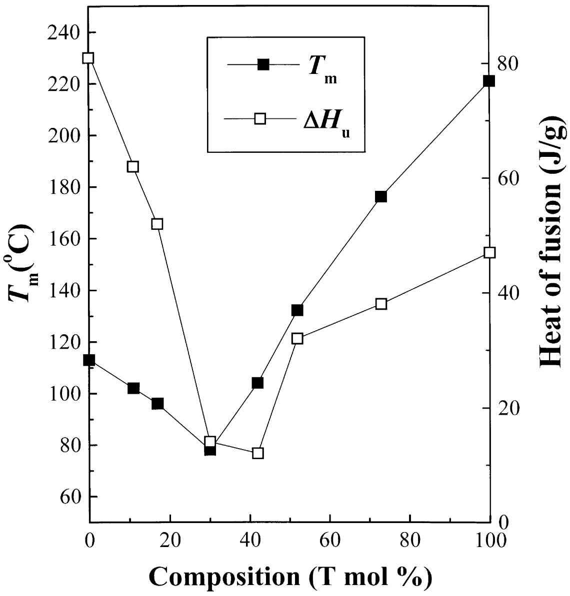

Fig. 2. Plot of T_m and ΔH_u values of copolymers measured by DSC versus copolymer composition.

2.3. Enzymatic degradation

The film specimen (20 mm × 20 mm, about 120 μm thickness) was placed in a small bottle containing 10 ml of 1/15 mol phosphate buffer solution (pH 7.2) with or without 20 mg of *Rhizopus delemar* lipase (fine grade from Seikagaku Kogyo Co. 720 unit/mg). The bottle was then incubated at 37°C for various times. After incubation the film was washed with water thoroughly and dried overnight at room temperature in vacuo. The degree of degradation was estimated from the weight loss expressed by g/m^2.

3. Results and discussion

Table 1 shows the molar composition in copolymers as-prepared and reduced specific viscosities (η_{sp}/C). These copolymers have relatively higher η_{sp}/C values, thus formed flexible and tough films by melt-pressed method. The molar composition in copolymers was determined by ^{1}H NMR. The peaks of proton due to methylene group in succinic acid and benzene ring in terephthalic acid appeared at 2.6 and 8.1 ppm, respectively, and their relative intensities were used to calculate the composition. The composition in the copolymers is in good agreement with those expected from the composition in feed.

DSC analyses was performed on melt-quenched samples. Glass transition temperature (T_g), melting temperature (T_m) and heat of fusion (ΔH_u) of copolymers are plotted against the copolymer composition in Figs. 1 and 2, respectively. T_g increases monotonically with an increase in the T content. The solid curve in Fig. 1 shows the curve predicted from Wood's equation [5] of $T_g = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2)$,

Table 2
Tensile properties and crystallinity of copolymer films

Polymer code	Tensile strength (kg/mm^2)	Elongation (%)	Young's modulus (kg/mm^2)	Crystallinity (%)[a]
T-0	2.1	116	52.6	73
T-11	2.2	415	33.1	56
T-17	1.8	371	25.2	47
T-30	1.9	447	16.0	43
T-42	1.3	590	7.4	11
T-52	1.4	364	10.9	29
T-73	2.4	6.8	58.2	35

[a] Estimated by dividing the observed heat of fusion by theoretical value (110.3 J/g) for pure 4G4.

where T_{g1}, T_{g2} and w_1, w_2 are the T_gs and weight fractions of succinic acid and terephthalic acid monomer units, respectively, T_g is glass transition temperature of the copolymer, and k represents the ratio of the volume expansion coefficients of the components at the T_g. T_g values of copolymers are well fitted by Wood's equation with $k = 0.36$. The melting point–composition curve shows the minimum at T-30 usually observed with random copolymer system [6]. ΔH_u decreases drastically with an increase in the T content, suggesting that crystal growth of 4G4 is disturbed by the incorporation of the T component. The crystallinity of the polymers has been frequently determined by dividing the observed ΔH_u values by the theoretical value for 100% crystalline polymer. The theoretical ΔH_u value for 4G4 was 110.3 J/g calculating on the basis of the group contribution method proposed by Van Krevelen [7]. Relative crystallinities of the copolymers thus estimated were 73% for 4G4, 56% for T-11, 47% for T-17, 13% for T-30, 11% for T-42, 29% for T-52 and 35% for T-73, which are listed in Table 2. The results of tensile tests are summarized in Table 2. Tensile strength decreases slightly and the Young's modulus decreases largely with increasing T content except for the case of T-73. Copolymerization also gives the larger elongation except for the case of T-73. Larger elongation and smaller Young's modulus may be responsible for the markedly reduced crystallinity mentioned above.

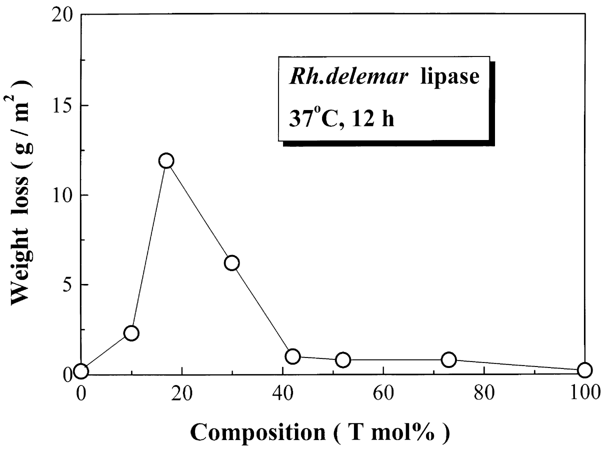

Fig. 3. Plot of weight loss of copolymer films degraded in the phosphate buffer solution of *Rh. delemar* lipase at 37°C for 12 h versus copolymer composition.

The degradation of copolymer films was performed in the phosphate buffer solution with *Rh. delemar* lipase at 37°C. The weight loss increased almost linearly with time for 24 h. In the absence of a lipase weight loss was hardly observed for the same incubation period. Fig. 3 shows the dependence of weight loss on the composition of copolymer when the sample is degraded for 12 h. It would be expected that the rate of degradation decreases with increasing T content because the aromatic ester linkage is less degradable than aliphatic ester one by *Rh. delemar* lipase [1]. However, T-17 gives the maximum weight loss. This large enhancement of degradation rate for T-17 film would be ascribed to the large decrease of the crystallinity of 4G4 unit described above.

T-17 film, degraded most rapidly by *Rh. delemar* lipase enzyme as described above, was drawn uniaxially at 40°C with a draw ratio of three times in order to improve the mechanical properties. The tensile properties, thermal properties, crystallinity and enzymatic degradability of T-17 film before and after the drawing are summarized in Table 3. As expected, the drawing results in a large increase in the tensile strength and a decrease in the elongation. The weight loss of the drawn T-17 film reduces appreciably. As mentioned above, the degree of crystallinity in this copolymer is a dominant factor for determining the enzymatic degradability. Since the crystallinity of the drawn film is almost the same as that of the undrawn film, the crystallinity itself does not directly affect the degradation. The other factors of orientation and surface morphology would affect the enzymatic degradability of the drawn films. After the amorphous region on the film surface is degraded, the film surface is rich in crystal layer. The half-maximum width of the principal diffraction peak (110) at $2\theta = 22.5°$ estimated by the wide angle X-ray diffraction pattern was somewhat smaller for the drawn film than that of the undrawn one, implying the crystallite alignment parallel to the film surface, which may decrease the rate of degradation. The research on the effects of these factors is now in progress. It is, indeed, noteworthy that tensile strength and enzymatic degradation rate of 4G4 was greatly enhanced by the copolymerization of T the component.

Table 3
Comparison of tensile properties, thermal properties, crystallinity and weight loss for T-17 film before and after drawing with three times drawing ratio at 40°C

	Tensile strength (kg/m^2)	Elongation (%)	Young's modulus (kg/m^2)	T_m (°C)	Heat of fusion (J/g)	Crystallinity (%)[a]	Weight loss (g/m^2)[b]
Before drawing	1.8	371	25.2	93	52	47	12
After drawing	5.7	63	31.5	93	51	46	6.7

[a] Estimated by dividing the observed heat of fusion by theoretical value (110.3 J/g) for pure 4G4.
[b] Degraded in a buffer solution of *Rh. delemar* lipase at 37°C for 12 h.

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