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BIODEGRADABILITY OF COPOLYESTERAMIDES FROM HEXAMETHYLENE ADIPATE AND HEXAMETHYLENEADIPAMIDE

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Abstract—A series of copolyesteramides (E66/A66) were prepared by a melt polycondensation from hexamethylene glycol (E6), hexamethylenediamine (A6), and adipic acid (6). Spacing measured by WAXS showed the discontinuous change at the copolymer composition of A66 = 20 mol.%. Melting temperature (T_m) of A66 decreased continuously with increasing E66 component, while T_m of E66 increased by the copolymerization of A66 component, suggesting the partial isomorphism. Degree of crystallinity estimated by WAXS and the heat of fusion estimated by DSC decreased by the copolymerization and showed a minimum at the copolymer composition of A66 = 20 mol.%. Solubility in various solvents decreased and thermal stability estimated by thermogravimetry increased with increasing A66 component. The biodegradability of E66 increased very rapidly by the copolymerization up to 20 mol.% of A66 component and then decreased very rapidly with increasing A66 component. The weight loss in aqueous solution of a lipase at 37° for 18 hr is 5.0 and 56.5 g/m^2 for E66 homopolymer and E66/A66(80/20) copolymer, respectively. This much higher biodegradability of copolymer could be explained by the large decrease of crystallinity. The weight loss by alkali hydrolysis increased up to 60 mol.% of A66 component and then decreased with increasing A66 component.

INTRODUCTION

There has been an increasing interest for the development of synthetic biodegradable polymers, because the problem of plastic wastes has been severe all over the world. Among synthetic polymers, aliphatic polyesters have been shown to be degradated by several commercial lipases and hog liver esterase [1]. However, the aliphatic polyesters generally have a low melting point and inferior mechanical strength, which makes their utilization as a material in various fields difficult. On the other hand, aliphatic polyamides (nylons) have a high melting point and superior mechanical properties, but have no biodegradability except for their oligomers [2, 3]. Thus it is expected that biodegradable polyesteramides having higher thermal and mechanical properties could be prepared by the copolymerization of aliphatic polyesters with nylons. However, the biodegradability of polyesteramides have been little examined [4, 5].

In this study, a series of random copolyesteramides are prepared from hexamethylene glycol and hexamethylenediamine with adipic acid, which have been previously prepared by Goodman *et al.* [6]. The enzymatic degradation is measured in an aqueous solution of a lipase and the effect of copolymer composition on the enzymatic degradation is investigated systematically compared with the alkali hydrolysis.

EXPERIMENTAL

Materials

Adipic acid, hexamethylene glycol and tetraisopropyl titanate (catalyst) were obtained commercially and were used without further purification. Hexamethylenediamine was distilled under reduced nitrogen atmosphere. Rhizopus delemar lipase (fine grade) was purchased from Seikagaku Kogyo Co. Ltd and used as received.

Polymerization

The following polycondensation procedure is representative for the preparation of copolymers containing ⩽40 mol.% of hexamethyleneadipamide component. 20 mmol of adipic acid and 20.4 mmol of a mixture of hexamethylene glycol and hexamethylenediamine in the presence of tetraisopropyl titanate (approx. 0.5% of the total weight) were heated in a glass vessel at 190° for 2 hr. Then the mixture was heated up to 220–230° and subjected to continue heating at the same temperature for 3 hr under vacuum below 1 torr.

For copolymers containing ⩾50 mol.% of hexamethyleneadipamide component, a general procedure is as follows. The mixture with the similar composition described above was heated at 200–240° (depending on composition of copolymers) for 2 hr. Then the temperature was raised up to 260° and maintained at the same temperature for 0.5–3 hr under vacuum below 1 torr.

Film preparation

Film specimen was prepared by casting about 15% solution of copolymer in formic acid on a glass plate. Solvent evaporation was conducted in a draft chamber and the residue was removed by heating the films under vacuum at 40° for 24 hr.

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Characterization

Reduced specific viscosity was determined with a 1% polymer concentration in *m*-cresol at 30° using an Ubbelohde type viscometer. IR spectrum was recorded on a Shimadzu model IR-408 spectrophotometer using a thin film. WAXS pattern was obtained for film specimens using a Rigaku Denki RAD-IA X-ray diffractometer with Ni filtered CuK_α radiation. The diffractograms were separated into crystalline and amorphous regions (O_c and O_a) and crystallinity (X_c) was calculated from the simple relation: $X_c = 100\ O_c/(O_c + O_a)$. Differential scanning calorimetry (DSC) and thermogravimetry (TG) was performed in nitrogen atmosphere with a Shimadzu thermal analyser DSC-50 and TG-30, respectively. A heating rate was 10°/min for DSC and 20°/min for TG. Tensile properties were measured with a Shimadzu Autograph IM-100 at a strain rate of 100%/min. Solubility of 10 mg of polymers was examined in a 0.5 ml of solvent.

Enzymatic degradation

The biodegradability of copolymer was assayed by the weight loss when an enzyme acted on it. The film specimen (initial film dimension size 20 × 20 mm and about 150 μm thickness) was placed in a small bottle containing 10 ml of 1/15 mol phosphate buffer solution (pH 7.2) and 20 mg of Rhizopus delemar lipase. The bottle was then incubated at 37° for various times with shaking. After incubation the film was washed with water and dried at 40° for 24 hr to constant weight, and its weight was determined.

Alkali hydrolysis

Alkali hydrolysis of copolymer was conducted in a 10% sodium hydroxide aqueous solution at 40° for various times and the weight loss was measured. The size and thickness of the film specimens was the same as that used in previous enzymatic degradation.

RESULTS AND DISCUSSION

A series of copolyesteramides (E66/A66) were prepared from adipic acid (6), hexamethylene glycol (E6) and hexamethylenediamine (A6) by a melt polycondensation method using a catalyst. Compositions and reduced specific viscosities (η_{sp}/C) are summarized in Table 1. The composition of copolymers was calculated on the basis of nitrogen content obtained by elemental analysis. Monomer feed ratio agrees well with the composition in copolymer. η_{sp}/C of copolymers indicates that copolymers of reasonably high molecular weight were obtained.

Table 1. Composition and reduced specific viscosity of copolymers

Composition of A66 (mol.%)		
Composition in feed	Composition in copolymer	η_{sp}/C* (dl/g)
0	0	0.84
10	9	1.08
20	20	0.79
30	31	0.88
40	42	1.15
50	51	0.76
60	62	0.96
70	73	0.78
80	80	0.92
90	91	1.21
100	100	1.39

*0.1 g/ml in *m*-cresol at 30°C.

Figure 1 shows representative IR spectra of copolymers. The major absorptions characteristic of the amide group appeared at 1640 cm^{-1} (C=O stretching) and 1540 cm^{-1} (NH bending), respectively, and those of ester group at 1740 cm^{-1} (C=O stretching) and 1170 cm^{-1} (C—O anti-symmetry stretching), respectively. The composition of copolymer can also be obtained from the ratio of IR absorbances at 1640 cm^{-1} (h_1) and 1740 cm^{-1} (h_2). The values of $h_1/(h_1 + h_2)$ vs compositions obtained from elemental

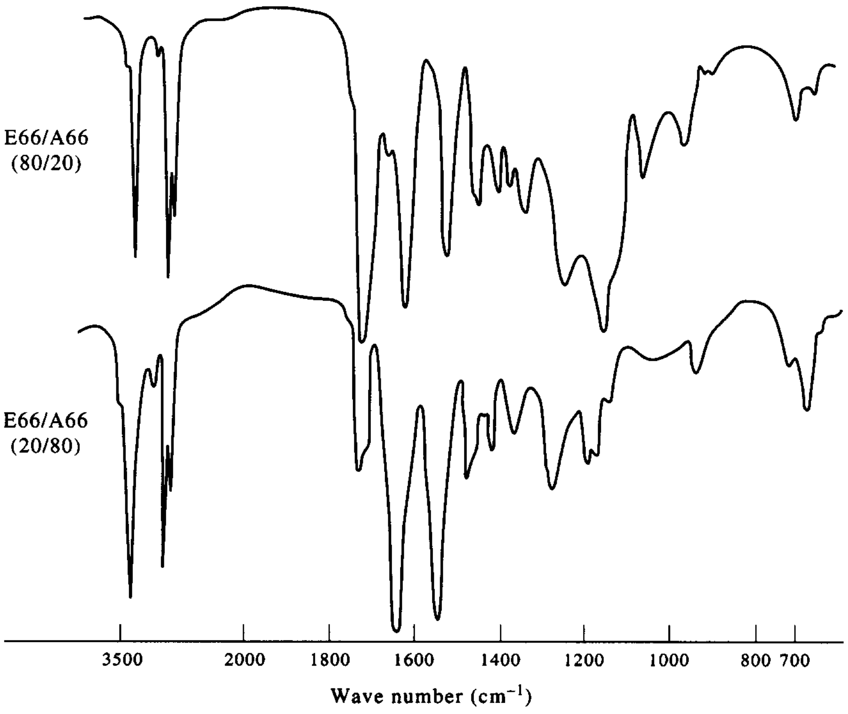

Fig. 1. Infrared spectra of copolymers.

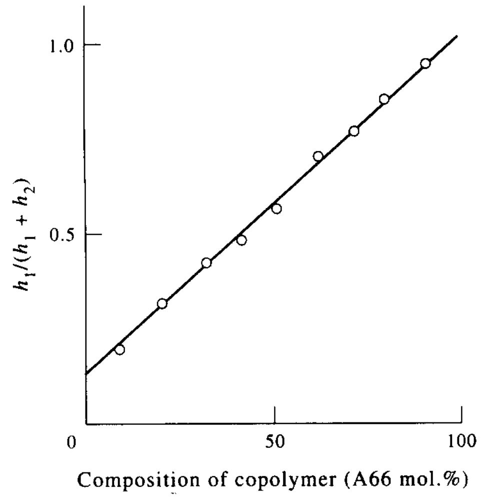

Fig. 2. Infrared/composition calibration curve for copolymers. h_1: absorbance at 1640 cm^{-1}; h_2: absorbance at 1740 cm^{-1}.

Table 2. T_g* and T_{cc}† of copolymers

Polymer	T_g (°C)	T_{cc} (°C)
A66	42	63
E66/A66 (10/90)	35	55
E66/A66 (20/80)	<30	40

*Glass transition temperature.
†Cold crystallization temperature.

analysis are shown in Fig. 2. A linear relationship is obtained between them.

The structural resemblance between amide and ester moiety in E66/A66 copolymer might afford a possibility to form isomorphous crystal. Izard [7] reported that copolyesteramide prepared from hexamethylene sebacate and hexamethylenesebacamide forms isomorphous crystal since T_m vs a composition relationship displayed no eutectic minimum. However, the spacing of crystal lattice was not measured. The values of spacing (d) of principal reflections estimated from WAXS patterns are plotted against the composition of copolymers in Fig. 3. There is no noticeable shift for the (210) spacing of 4.31 Å of E66 or (100) spacing of 4.29 Å of A66 when the composition is varied, which is probably because this spacing of both homopolymers is nearly identical. On the contrary, the (010) spacing of 3.63 Å of A66 is approximately constant up to 30 mol.% of A66 component, and then shifts toward the (020) spacing of 3.80 Å of E66. This discontinuous change of spacing implies that E66/A66 copolymer system could not form isomorphous crystal.

The values of melting point (T_m) for films against the composition of copolymers are plotted in Fig. 4. T_m increases with increasing A66 component with the discontinuous change at the composition between 20 and 30 mol.% of A66 component, which corresponds well to the discontinuous change of the spacing shown in Fig. 3. The increase of T_m for the copolymers containing 10 and 20 mol.% of A66 component suggests that these copolymers are partially isomorphous in spite of the fact that the spacing of these copolymers hardly changed.

The glass transition temperature (T_g) and cold crystallization temperature (T_{cc}) were measured for melt-quenched dry samples. The results are summarized in Table 2. The introduction of E66 component into A66 leads to the decrease of T_g, which was not observed for copolymers containing <80 mol.% of A66 component since DSC commenced from room temperature. The T_{cc} values also decrease with increasing E66 component, suggesting that the more flexible E66 chain causes crystallization of the A66 component at a lower temperature.

The crystallinities determined by WAXS patterns are plotted against the composition of copolymers in Fig. 5. The copolymers are crystalline over the whole range of composition. The crystallinity of E66 decreases rapidly and that of A66 decreases gradually with a minimum at 20 mol.% of A66 component. The values of heat of fusion (ΔH_u) as a measure of relative crystallinity determined by DSC are also plotted against compositions of copolymers in Fig. 6. The variation of crystallinity shown in Fig. 5 is almost comparable to that of ΔH_u in Fig. 6.

Table 3 summarizes the solubilities of copolymers in various solvents. The solubility decreases with increasing A66 component. This may be due to the strong hydrogen bonding force in polyamide moiety.

Figure 7 shows the TG curves of E66 and A66 homopolymers, and E66/A66(50/50) copolymer. E66 homopolymer decomposes at a much lower temperature than A66 homopolymer. Decomposition starting temperatures of the copolymers were between both homopolymers and increased with increasing A66 component due to the higher thermal stability of polyamide.

Table 3. Solubility of copolymers*

	Composition of copolymer (A66 mol.%)										
Solvent†	0	10	20	30	40	50	60	70	80	90	100
DMAc	+ +	+ +	+ +	+ +	+	+	+	+	+	+	−
DMF	+ +	+ +	+ +	+ +	+	+	+	+	+	−	−
NMP	+ +	+ +	+ +	+ +	+	+	+	+	+	+	−
DMSO	+ +	+ +	+ +	+ +	+	+	+	+	+	+	+
m-Cresol	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Formic acid	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Dioxane	+ +	+ +	+ +	+	−	−	−	−	−	−	−
Tetrahydrofuran	+ +	+ +	−	−	−	−	−	−	−	−	−
Chloroform	+ +	+ +	+	+	+	−	−	−	−	−	−
Methylene chloride	+ +	+ +	−	−	−	−	−	−	−	−	−

*+ +: Soluble cold; +: soluble hot; −: insoluble.
†DMAc: *N*,*N*-dimethylacetamide; DMF: *N*,*N*-dimethylformamide; NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethylsulfoxide.

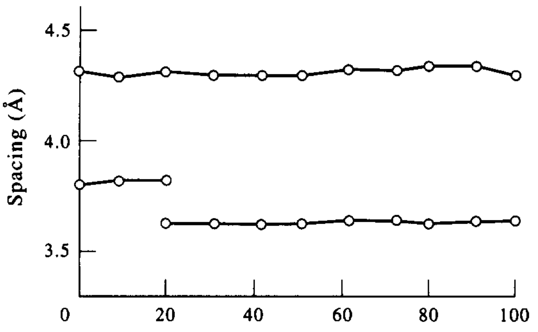

Fig. 3. Spacing against composition of copolymers.

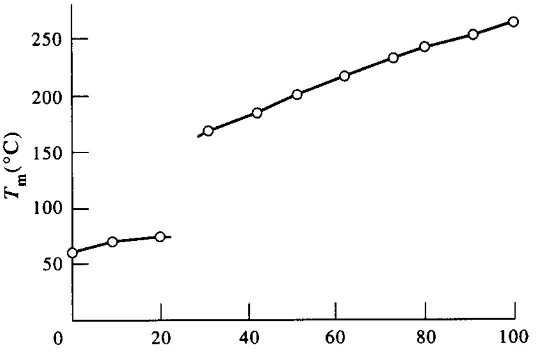

Fig. 4. Melting point against composition of copolymers.

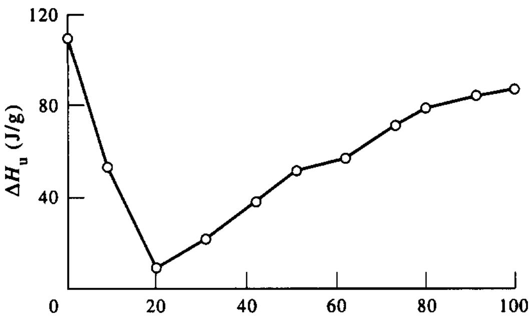

Fig. 6. Heat of fusion against composition of copolymers.

Tensile strength, elongation and Young's modulus were 1.0 kg/mm^2, 3% and 49 kg/mm^2 for E66 homopolymer, and 1.0 kg/mm^2, 350% and 5 kg/mm^2 for E66/A66(80/20) copolymer, respectively. The much higher elongation and much lower Young's modulus of E66/A66(80/20) copolymer is presumably attributed to the larger decrease of crystallinity of this copolymer as shown in Fig. 5. Tensile strength did not decrease by the copolymerization, which suggests the effect of intermolecular hydrogen bonding formed by the nylon moiety.

The enzymatic degradation of copolymers was examined in aqueous solution of a lipase at 37°. Figure 8 shows the weight loss of E66/A66(80/20) copolymer against degradation time. The weight loss increases with time, showing a typical parabolic-type degradation pattern [8]. Figure 9 shows the weight loss of copolymer degradated at 37° for 18 hr against the composition of copolymer. The weight loss increases very rapidly up to 20 mol.% and then decreases very rapidly with increasing A66 component. The weight loss was hardly observed in the copolymer containing >60 mol.% of A66 component. Tokiwa *et al.* [4] showed that the biodegradability of block copolyesteramides prepared by the ester–amide interchange reaction between polycaprolactone and nylons decreases with increasing nylon moiety. Since a lipase cleavages only ester bond, E66 homopolymer is expected to be most susceptible to

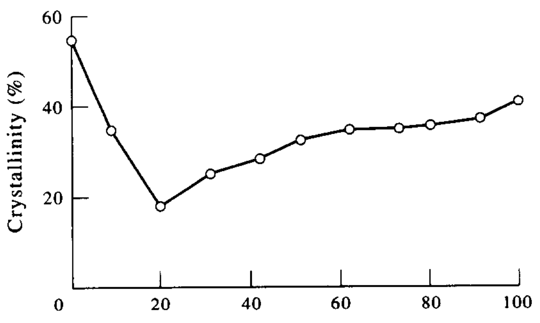

Fig. 5. Crystallinity against composition of copolymers.

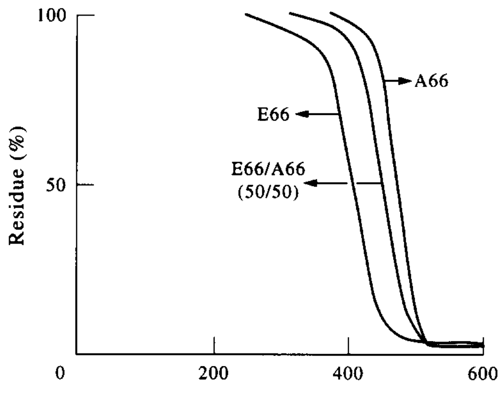

Fig. 7. TG curves of E66 and A66 homopolymers and E66/A66(50/50) copolymer.

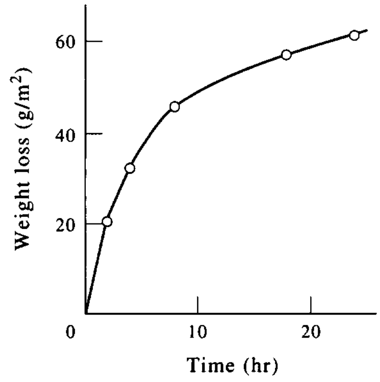

Fig. 8. Weight loss of E66/A66(80/20) copolymer against degradation time in aqueous solution of a lipase at 37°.

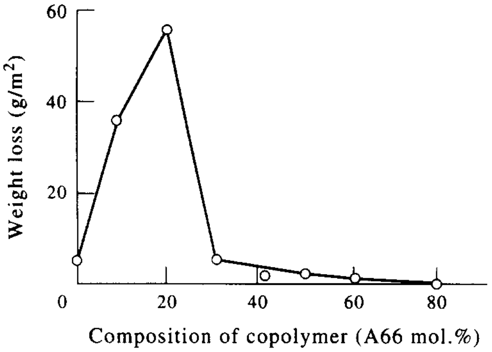

Fig. 9. Weight loss against composition of copolymers in aqueous solution of a lipase at 37° for 18 hr.

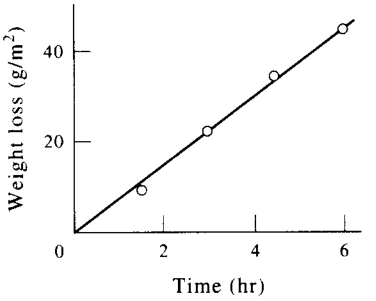

Fig. 10. Weight loss of E66/A66(40/60) copolymer against hydrolysis time in a 10% sodium hydroxide aqueous solution at 40°.

enzymatic degradation. However, the weight loss of E66 homopolymer is much smaller than those of E66/A66(90/10) and E66/A66(80/20) copolymers. This is probably because the decrease of crystallinity for these copolymers, as shown in Fig. 5, accelerates the enzymatic degradation of them, and thus E66/A66(80/20) copolymer having the lowest crystallinity shows the highest weight loss. It is noteworthy that the biodegradability is greatly affected by the crystallinity of polymer.

Alkali hydrolysis of copolymers has been also examined in order to compare with enzymatic degradation previously described. Figure 10 shows weight loss of E66/A66(40/60) copolymer against times in a 10% sodium hydroxide aqueous solution at 40°. The weight loss increases linearly with time. Figure 11 shows the weight loss of copolymer hydrolysed in a 10% sodium hydroxide aqueous solution at 40° for 6 hr against the composition of copolymer. The weight loss increases whilst increasing up to 60 mol.% of A66 component, suggesting that alkaline hydrolysis is affected by the content of hydrophilic amide moiety which could accelerate the permeation of alkali aqueous solution into the film. The decrease of weight loss with increasing A66 component may be attributed to the decrease of ester linkage.

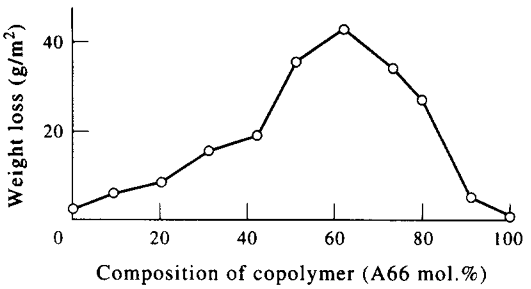

Fig. 11. Weight loss against composition of copolymers in 10% sodium hydroxide aqueous solution at 40° for 6 hr.

It is concluded that the higher biodegradable, higher melting and higher thermal and chemical resistant polymers could be prepared by the incorporation of isomorphous nylon moiety into aliphatic polyesters.

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