Biodegradable elastic photocured polyesters based on adipic acid, 4-hydroxycinnamic acid and poly(ε-caprolactone) diols

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Abstract

A novel series of photocurable biodegradable polyesters (CAC/PCL) were synthesized by a high-temperature solution polycondensation of poly(ε-caprolactone) (PCL) diols varying molecular weight (M_W; 1250, 2000, 3000) and a diacyl chloride of 4,4′-(adipoyldioxy) dicinnamic acid (CAC) as a chain extender derived from adipic acid and 4-hydroxycinnamic acid. The resulting polyesters were photocured by the ultraviolet (UV) light irradiation ($\lambda > 280$ nm) in order to prepare elastic polyester with enhanced thermal and mechanical properties. The effects of photocuring by the UV light irradiation on the thermal, tensile and hydrolytic properties of the CAC/PCL were examined. DSC indicated that the melting temperatures and the crystallinities are decreased by the photocuring. The tensile properties of the photocured CAC/PCL films depended on the M_W of PCL-diols and photocured time. The CAC/PCL1250 films photocured for 10–60 min exhibited a strength-at-break of 3.1–4.7 MPa and an elongation-at-break of 640–1500%, and recovered very rapidly to the original size from 90 to 300% extension. Enzymatic degradation was performed in the phosphate buffer solution (pH 7.2) with *Ps. cepacia* lipase at 37 °C and evaluated by the weight loss. Non-photocured CAC/PCL films were degraded very rapidly and the weight loss after 3 h incubation was more than 60%. The weight loss of the photocured films decreased remarkably with increasing the photocuring time due to the increase of cross-linking density, while it increased with increasing the M_W of PCL-diols. The photocured CAC/PCL1250 film is promising as a novel biodegradable elastomer for biomedical applications as well as environmental applications.
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Keywords: Elastic photocured polyesters; Biodegradable; Poly(ε-caprolactone)diols

1. Introduction

Many investigations on synthesis, properties and degradability of biodegradable polymers have been made during the past decades. Aliphatic polyesters such as poly(glycolic acid) (PGA), poly(L-lactic acid) (PLLA), poly(ε-caprolactone) (PCL), and poly(1,4-butanediol succinate) (PBS) are the most extensively investigated because of their good biodegradability and suitable properties [1]. However, they lack the physical and mechanical properties for increasing the scopes of environmental as well as biomedical applications.

By introducing crosslinks into a polymer chain, physical properties such as the crystallinity, the melting point, the glass transition temperature and solubility would be affected. These physical properties would also affect the

biodegradability of polymers. The mechanical properties such as tensile strength, impact strength and modulus of polymers would be enhanced by the crosslinking, which is very important in environmental applications as well as biomedical applications. Furthermore cross-linked polymers have potentials for a wide range of applications including biodegradable elastomers, hydrogels and adhesives. The crosslinkings of biodegradable polymers by chemical initiators [2–4] or γ-irradiation [5–8] have been reported by several researchers. The incorporating cinnamoyl group into the polymer chains would be a convenient way to produce the crosslinkable biodegradable polymers since polycinnamates can be readily photochemically crosslinked [9]. In addition, the cinnamoyl group is metabolized in the body and has been proven to be non-toxic [10]. A few biodegradable hydrogels have been prepared by photocrosslinking hydrophilic copolymers containing the pendent or terminal cinnamoyl group in the polymer chains [11,12]. But, there have been few reports on the photocrosslinkings

of biodegradable polyesters containing the cinnamoyl group in the main chain. Recently, biodegradable photocrosslinkable copolyesters composed of 4-hydroxycinnamic acid (HCA) and DL-lactic acid have been prepared [13]. We have synthesized the biodegradable polyesters based on adipic acid, HCA and poly(ethylene glycol)s, which were photocured to yield the hydrogels [14].

In this article, we synthesized the novel photocurable biodegradable polyesters from poly(ε-caprolactone)diols of various molecular weight (M_W) and 4,4'-(adipoyldioxy)-dicinnamic acid (CAC) as a chain extender, which was derived from 4-hydroxycinnamic acid and adipic acid. The aim of the present study is to prepare biodegradable elastic polyesters with enhanced thermal and mechanical properties. The effects of the photocuring on the thermal and mechanical properties as well as enzymatic degradation were investigated systematically.

2. Experimental

2.1. Materials

4-Hydroxycinamic acid (HCA) was purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. Diphenyl oxide was distilled under vacuum prior to use. Adipoyl chloride was synthesized by refluxing a mixture of adipic acid and thionyl chloride, followed by the distillation in vacuo. The other reagents such as chloroform and n-hexane were purified by the standard procedure. 4,4'-(Adipoyldioxy)-dicinnamic acid (CAC) and diacyl chloride of CAC were synthesized as described in the previous paper [14]. Poly(ε-caproactone) ($M_n = 50,400$, $M_w/M_n = 1.55$, polystyrene standards) was gifted from Daicel Chemical Co. Ltd. Poly(ε-caprolactone) diols (PCL-diol) [α-ω-dihydroxy poly(ε-caprolactone)] of the number average molecular weight of 1250, 2000 and 3000 were supplied by Aldrich Co. Ltd with the following formula: H[−O(CH$_2$)$_5$CO−]$_n$O(CH$_2$CH$_2$O)$_2$ [−CO(CH$_2$)$_5$O−]$_m$H.

These prepolymers were dried over P_2O_5 at ambient temperature in vacuo.

2.2. Polymerization

Polyesters were prepared by a high-temperature solution polycondensation in diphenyl ether. A typical procedure is described as follows. A mixture of 1 mmol (0.475 g) of CAC dichloride, 1 mmol (1.25 g) of PCL1250-diol and 15 ml of diphenyl oxide was introduced into three-necked round-bottomed flask equipped thermometer, magnetic stirrer and drying tube, continuing a dry nitrogen flow. The temperature was raised to 180 °C over 30 min and the reaction was continued at the same temperature for 2 h. After the flask was cooled, viscous solution was poured into 75 ml of cold n-hexane. The precipitated polymer was filtered off, and reprecipitated from chloroform into cold n-hexane and dried in vacuo at room temperature. Yield, 85%.

FTIR (film) cm^{-1}: 2943, 2867 (CH stretching); 1734, 1760 (ester C=O), 1637 (C=C), 1602, 1508 (aromatic C−C), 1111, 1128, 1167, 1207 (C−O−C). ^{1}H NMR (CDCl$_3$) $\delta = 1.55-1.77$ (−COCH$_2$(CH$_2$)$_2$CH$_2$CO− and −CH$_2$(CH$_2$)$_3$CH$_2$CO− of PCL), 2.27−2.35 (−COCH$_2$(CH$_2$)$_2$CH$_2$−CO− and −CH$_2$−CO− of PCL), 4.03−4.17 (−CH$_2$O− of PCL), 6.30−6.48 (CH=CHPh). 7.07−7.16 (Ph, meta to CH=CH), 7.49−7.54 (Ph, ortho to CH=CH), 7.57−7.75 (CH=CHPh).

2.3. Film preparation

The CAC/PCL films of about 200−220 μm were prepared by melt-pressing at 40−70 °C, and subsequent quenching in ice-cooled bath, and then dried in vacuo at room temperature for 24 h.

2.4. Characterization

Gel permeation chromatography (GPC) was carried out on a Waters system. A set of Waters Styragel columns (HR 1, HR 2, and HR 4) were connected in series and operated at a flow rate of 1 ml/min in chloroform at 35 °C. Polystyrene standards with low polydispersities were used for calibration. Fourier transform infrared spectra (FTIR) were recorded on a JEOL JIR-Diamond20 spectro-photometer using a thin film on a KRS substrate. ^{1}H NMR spectra were obtained at 25 °C in CDCl$_3$ using a JEOL JNM-EX90A FT-NMR spectrometer with TMS as the internal standard. Differential scanning calorimetry (DSC) was performed at a heating rate of 10 °C/min in a nitrogen atmosphere with a Shimadzu DSC-50 differential scanning analyzer controlled by TA-50 work station. Thermogravimetry (TG) was performed on a Shimadzu TG-30 thermogravimetric analyzer with a heating rate of 20 °C/min in a nitrogen atmosphere. Wide angle X-ray diffraction (WAXD) were performed for film samples with a Rigaku Denki model RAD-IA X-ray diffractometer with nickel filtered Cu Kα radiation. Ultra-violet/visible (UV/Vis) spectra were recorded on a Shimadzu UV-2100 spectrophotometer. Tensile properties of film specimens (length, 10 mm; width, 5 mm; thickness, 0.20−0.22 mm) were performed at room temperature (20 ± 2 °C) using a Shimadzu AG-1 autograph equipped with a 1 kN load-cell, a crosshead speed of 20 mm/min. An average of five measurements were taken with no more than 15% deviation from the mean.

2.5. Photoirradiation and determination of gelation

The photoirradiation was conducted using a 400 W high pressure mercury lamp (SEN LIGHT Co. Ltd.; Osaka, Japan) with a water jacket through a Pyrex cooler to cut off wavelength below 280 nm. The UV light intensity was

measured on a photometer (SPECTRONICS DRC100X, NY).

The melt-pressed CAC/PCL films (ca. 200–220 μm) were irradiated by the UV light (1.0 mW/cm^2). After the irradiation, the film was weighed (W) and immersed in chloroform for 24 h, then washed extensively with fresh chloroform to remove the unreacted soluble part of the polymer, and the gel was dried in vacuo and weighed (W_g). The gel fraction was calculated as $100 \times W_g/W$.

2.6. Enzymatic degradation

The film specimen (10 mm × 10 mm, ca. 200–220 μm thickness) was placed in a small bottle containing 10 ml of 1/15 mol phosphate buffer solution (pH 7.2) with and without 200 unit/ml of *Ps. cepacia* lipase (from Amano Pharmacy Co., Ltd. 1,000 unit/mg). The bottle was incubated at 37 °C for various periods of time. After incubation the film was washed with water and dried at 40 °C in vacuo. The degree of degradation was estimated from the weight loss, which was calculated using the following equation: Weight loss(%) $= 100(W_0 - W_t)/W_0$, where W_0 and W_t are the dry sample weight before and after the enzymatic degradation. The weight loss averaged for two specimens was employed.

3. Results and discussion

3.1. Synthesis of photocurable polyesters

Scheme 1 shows the preparative route of the novel photocurable polyesters (CAC/PCL). The use of a chain extender containing HCA component could introduce photoreactive double bond into the polymer backbone. Owing to the reactivity of cinnamic group, the conventional high-temperature melt polycondensation would be undesirable for the synthesis of such polymers since higher temperature potentially causes thermal crosslinking of double bonds and/or thermal degradation [15]. Hence the solution polycondensation of a diacyl chloride of CAC and
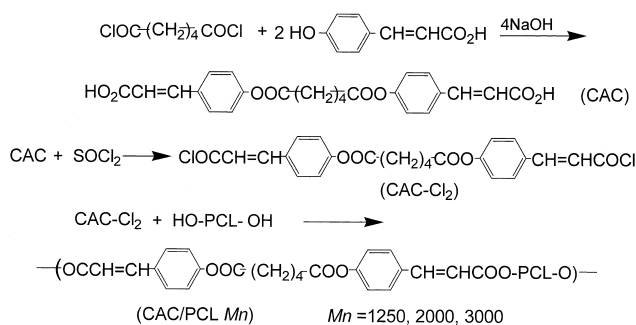
Scheme 1. Preparation of polyesters derived from adipic acid, 4-hydoxycinnamic acid and poly(ε-caprolactone) diols.

PCL-diol in a suitable solvent was used to obtain high molecular weight polyesters. The results of polycondensation are shown in Table 1. The higher molecular weight polyesters could be obtained successfully with good yields, which formed tough and flexible films by molding or casting. The number of average CAC/PCL repeating unit (n) in the polymer chain is in the 21–45 ranges, increasing with decreasing the M_W of PCL-diol.

The solubilities of the polyesters in organic solvents were determined. All the polyesters were readily soluble in most of the common organic solvents such as CH_2Cl_2, $CHCl_3$, DMF, DMSO, and aromatic solvents such as benzene and toluene, while insoluble in THF, acetone, ether, hexane, and methanol.

The structures of the polyesters were confirmed by FTIR and ^{1}H NMR. In a typical FTIR spectrum of a CAC/PCL1250 thin film, aliphatic C=C stretching conjugated with benzene ring appeared at 1637 cm^{-1}, suggesting that *trans* cinnamoyl group was successfully introduced into the polymer backbone. The *trans* isomerism of the double bond was also confirmed for all polyesters by ^{1}H NMR spectrum. Two doublet signals were appeared at 6.39 and 7.66 ppm with a coupling constant of 16 Hz, characteristic for *trans* cinnamoyl group.

3.2. Photoreactivity

The photoreactivity of CAC/PCL was examined in a film cast from a chloroform solution on a quarts plate at room temperature without a photosensitizer. Fig. 1(a) shows the changes in the absorption spectra for CAC/PCL1250 during increasing time of exposure to light. Cinnamate absorption maximum is observed at 283 nm, which shifts slightly to the lower wavelength and decreases with increasing the irradiation time, indicating that the cinnamoyl group could undergo a photochemical reaction in the film state. Cinnamoyl group is well known to (2 + 2) photocyclo-addition, resulting in the formation of cyclobutane ring [9,16]. After the irradiation, the film became insoluble in chloroform, the solvent from which it was cast. Fig. 1(b) shows the changes of the normalized absorption intensity (Abs$_t$/Abs$_0$) in the UV spectra of various CAC/PCL films with irradiation time, which was calculated by dividing the absorption intensity of the film photoirradiated for

Table 1
Yields and molecular weights of polyesters

Polymer code	Yield (%)	M_n[a]	M_w[a]	M_w/M_n[a]	n[b]
CAC/PCL1250	85	74,500	145,000	1.94	45
CAC/PCL2000	84	67,100	116,000	1.72	28
CAC/PCL3000	85	73,300	121,000	1.65	21

[a] Determined by GPC with polystyrene standards.
[b] The number of average repeating unit of CAC/PCL determined from the corresponding M_n values.
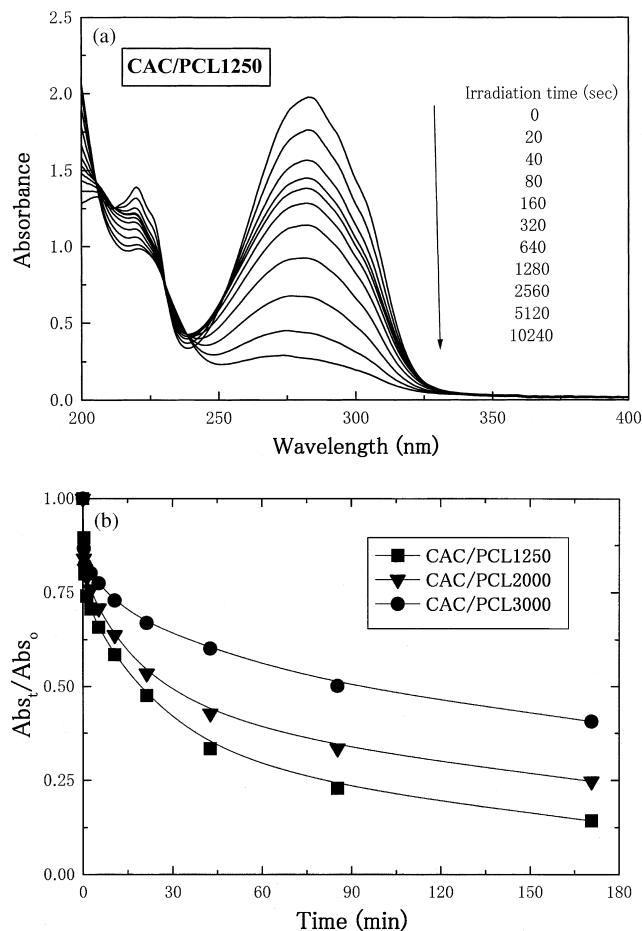
Fig. 1. (a) Changes of the UV/VIS spectra absorbance of CAC/PCL1250 thin film, (b) normalized absorbance of CAC/PCL films at 283 nm upon irradiation with 400 mW high pressure Hg lamp at ambient temperature. UV intensity: 0.35 mW/cm^2.

prescribed time by the initial absorption intensity of one. The photocrosslinking reaction occurred very rapidly at the early stage of photoirradiation. The fast initial decrease in absorption intensity is characteristic of a cross-linked polymer through the photodimerization because the concentration of cinnamoyl group is higher at the early stage. The rate of crosslinking reaction decreases in the order CAC/PCL1250 > CAC/PCL2000 > CAC/PCL3000, which would be responsible for the lower concentration of cinnamoyl groups in the polymer. The similar behaviors has been observed for the polymers prepared from CAC and poly(ethylene glycol) [14].

3.3. Thermal properties

DSC analyses were performed on melt-quenched CAC/PCL samples to remove the previous thermal history of the samples. The typical DSC heating curves of CAC/PCL showed the glass transition (T_g), cold crystallization exotherm (T_{cc}) and melting endotherm (T_m). These phase transition temperatures and heat of fusion (ΔH_m)

Table 2
Thermal properties of polyesters

Polymer code	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_m (J/g)	X_c [a] (%)
PCL[b]	−72	−61	55(60)[c]	69	51
CAC/PCL1250	−52	−33	31(38)	34	33
CAC/PCL2000	−58	−41	40(48)	46	41
CAC/PCL3000	−64	−48	46(53)	56	48

Determined for melt-quenched samples by DSC.

[a] Relative crystallinity calculated by means of the following equation: $X_c(\%) = 100 \cdot \Delta H_m / w \cdot \Delta H_m^0$ where ΔH_m^0 is the heat of fusion of 100% crystalline pure PCL (135 J/g) [17], ΔH_m is the heat of fusion of the sample, and w is the weight fraction of the PCL in the polymer.

[b] Supplied by Daicel Chemical Co. Ltd.

[c] Parenthesis shows T_m values for as-polymerized samples determined by DSC.

are summarized in Table 2. X-ray diffraction patterns of CAC/PCL exhibited the two sharp peaks at 22.3 and 24.7° of 2θ which was compatible with the pure PCL crystalline phase, indicating that the observed melting endotherm is due to the crystallizable PCL chain. The relative crystallinity of polymers (X_c) could be estimated with respect to PCL content in the polymer by means of

$$X_c(\%) = 100 \cdot \Delta H_m / w \cdot \Delta H_m^0$$

where ΔH_m^0 is the heat of fusion of 100% crystalline pure PCL (135 J/g) [17], ΔH_m is the heat of fusion of the sample, and w is the weight fraction of the PCL in the polymer. The calculated values are also included in Table 2. T_g values of CAC/PCL decrease with an increase of the M_W of PCL-diol, which would be ascribed to the larger content of PCL component. The T'_ms and X'_cs are lower than those of pure PCL, implying that the CAC moiety disturbs the crystal growth of PCL component.

The changes of thermal properties by the photocuring were followed by DSC and TG for CAC/PCL1250. Fig. 2
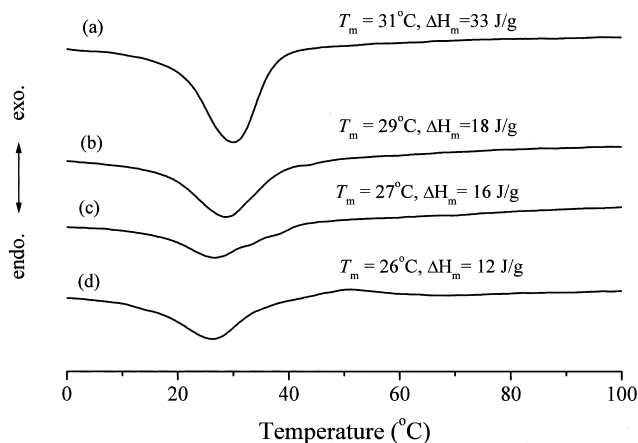

Fig. 2. DSC curves of CAC/PCL1250 melt-pressed films before and after photocuring. (a) non-photocured (b) photocured for 30 min (c) photocured for 60 min (d) photocured for 90 min.

shows DSC curves of melt-pressed films before and after the photocuring. The T'_ms and $\Delta H'_m$s are reduced gradually with photocuring time. After a 90 min curing (gel content 94%), ΔH_m value is reduced to about one third part of its initial value. The decrease of $\Delta H'_m$s indicates that the crosslinking reaction takes place in not only the amorphous region, but in the crystalline region.

The thermal stability of CAC/PCL1250 film before and after the photocuring was studied by a thermogravimetry performed in a nitrogen atmosphere. The TG curve before the photocuring exhibited a thermal decomposition starting temperature (1% weight loss temperature) (T_d) at 340 °C. T'_ds of the photocured films were in the range of 338–348 °C. The photocuring hardly affected the thermal stability of the films. The thermal stability of non-photocured film would be enhanced by the crosslinking of double bond in the polymer chains during the heating the sample. It has been reported that the higher temperature than 250 °C cause the thermal crosslinking of the cinnamoyl group [18].

3.4. Tensile properties

Table 3 summarizes the tensile properties before and after the photocuring along with gel contents for CAC/PCL films. In comparison those properties of the pure PCL film was determined. Fig. 3 shows the typical stress–strain curves of CAC/PCL1250 films. The gel contents increase with the photocuring time and show the values over 90% for all CAC/PCL films after 90 min irradiation. Before the photocuring, all films exhibited the characteristic yield
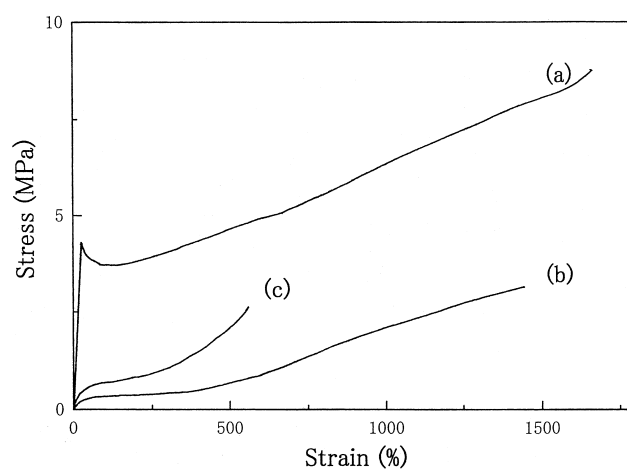

Fig. 3. Stress–strain curves of CAC/PCL1250 films before and after photocuring. (a) Non-photocured (b) photocured for 30 min (c) photocured for 60 min.

points of typical of plastic. The tensile strength and modulus of non-photocured CAC/PCL films are lower than those of pure PCL, which would be ascribed to the reduced crystallinity of the film shown in Table 2. The CAC/PCL1250 film shows the much higher maximum elongation of 1880%.

As expected, the elongation decreases remarkably with increasing the photocured time due to the increased degree of crosslinking. The CAC/PCL1250 films photocured for 10–60 min exhibited the elastic properties with the lower tensile strength and modulus. The film photocured for 90 min was not elastic, but brittle. The films photocured for 10, 30 and 60 min recovered very rapidly to the original size from ca. 90, 200 and 300% extensions, respectively. But, the elastic recoveries of these films were not perfect when they were further extended. These elastic properties would be caused by the flexible PCL component as the soft segment and the crosslinkings between the polymer chains through the formation of butane ring mentioned above, which suppress the slippage between the polymer chains. The degrees of elastic recovery increase with increasing the photocuring time, that is, the higher degree of crosslinking enhances the elastic properties of the films. In contrast, the photocured CAC/PCL2000 films exhibited elastic recoveries of only 30–50% and the photocured CAC/PCL3000 films hardly showed them. The much lower degree of elastic recoveries of CAC/PCL films with the higher M_W of PCL-diols may be ascribed to their higher crystallinities and melting temperatures compared with CAC/PCL1250 as shown in Table 2.

3.5. Enzymatic degradation

Enzymatic degradations were performed for non-photo-cured and photocured films using *Ps. cepacia* lipase, which has been reported to degrade ε-caprolactone homo-polymer readily [19]. Fig. 4 shows the weight losses of

Table 3
Gel contents and tensile properties of melt-pressed films before and after photocuring

Polymer code	Photocured time (min)	Gel content (wt.%)	Tensile strength (at break) (MPa)	Elongation (at break) (%)	Tensile modulus (MPa)
PCL[a]	–	–	14	830	68
CAC/PCL1250	0	–	8.7	1880	21
	10	28	3.1	1500	0.6
	30	52	4.7	1270	1.1
	60	70	3.8	640	4.4
	90	94	2.0	90	4.7
CAC/PCL2000	0	–	5.9	800	42
	10	15	5.7	760	37
	30	40	6.9	680	63
	60	75	6.4	450	26
	90	95	6.9	180	46
CAC/PCL3000	0	–	9.2	880	66
	10	5	7.0	840	58
	30	35	8.4	770	100
	60	75	6.9	420	76
	90	95	8.0	90	85

Film thickness; 200–220 μm. UV intensity; 1.0 mW/cm^2.
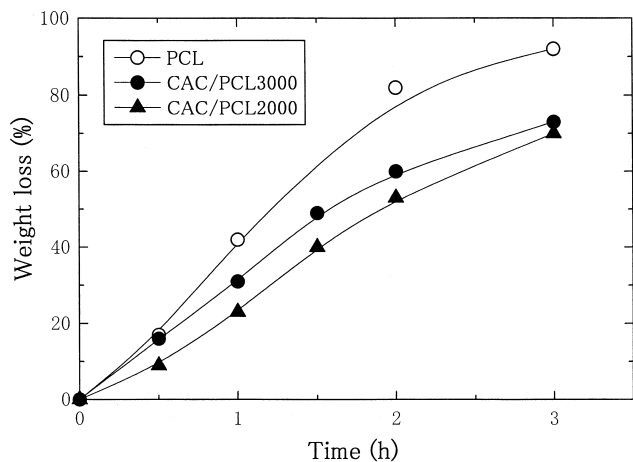[a] Supplied by Daicel Chemical Co. Ltd.

Fig. 4. Weight loss of CAC/PCL2000 and 3000 films before photocuring as a function of time of exposure to *Ps. cepacia* lipase.

non-photocured CAC/PCL3000 and CAC/PCL2000 films degraded in the phosphate buffer solution (pH 7.2) with *Ps. cepacia* lipase at 37 °C. Pure PCL film was also measured to compare the rate of degradation. The CAC/PCL1250 was not measured since its T_m is lower than the incubation temperature (37 °C). Weight losses increase very rapidly with time. All the films show the weight losses more than 60% after 3 h incubation. No weight loss was observed during the same period of incubation in the blank test for all the polyesters. These results indicate that the CAC/PCL2000 and 3000 as well as pure PCL are very easily degraded by *Ps. cepacia* lipase. The degradation rates of CAC/PCL 2000 and 3000 are slower than that of pure PCL, suggesting that the ester linkages between HCA and PCL-diol or adipic acid are less degradable than those in PCL component. The enzymatic hydrolysis products of by *Ps. cepacia* lipase was determined using a GPC. For the CAC/PCL1250 film sample after 24 h

incubation, the solution was freeze-dried and the residue was dissolved in tetrahyrofuran and filtered, then subjected to GPC analysis. Adipic acid, HCA, 5-hydroxycaproic acid along with some oligomeric products were detected, demonstrating that PCL/CAC polyester was degraded into monomers.

Fig. 5 shows the weight losses of the PCL/CAC1250 films photocured for various times degraded in the same conditions as the case of non-photocured films. The weight loss decreases significantly with increasing the photocuring time, which could be ascribed to the increased gel contents as shown in Table 3. It is worth noting that the cross-linked polyester films can be readily hydrolyzed by *Ps. cepacia* lipase. Fig. 6 shows the effects of M_W of PCL-diols on the rates of degradation of various CAC/PCL films photocured for 90 min (gel content, 94–95%). The weight losses increase remarkably with increasing M_W of PCL-diols. The similar behaviors were obtained for the CAC/PCL films photocured for 10–60 min. As the M_W of chains between crosslinks increases, the network space increases, which could facilitate the enzyme to penetrate into the film. Further the higher M_W of PCL-diols may favor the enzymatic degradation of the photocured films similarly to non-photocured films described above.

4. Conclusions

A series of high-molecular weight photocurable biodegradable polyesters were synthesized by a solution polycondensation of poly(ε-caprolactone) diols (PCL-diol) and CAC dichloride as a chain extender. The resulting polyesters could be easily photocured by the ultraviolet light irradiation ($\lambda > 280$ nm) without a photosensitizer. The CAC/PCL1250 film photocured for 10–60 min recovered very rapidly to the original size from 90 to
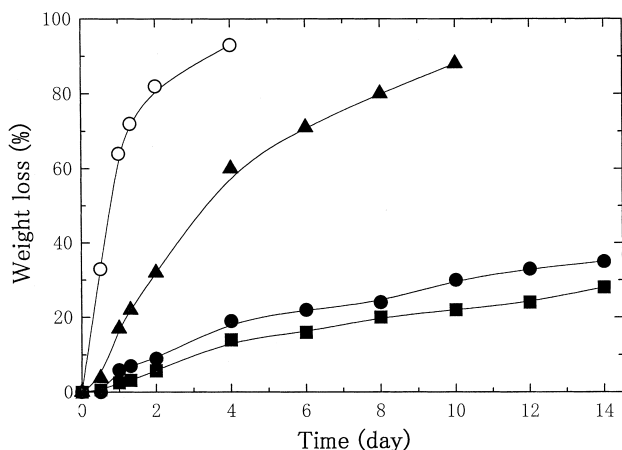

Fig. 5. Effect of photocuring time on weight loss of CAC/PCL1250 films as a function of time of exposure to *Ps. cepacia* lipase. Photocuring time: (○)10 min; (▲) 30 min; (●) 60 min; (■) 90 min.
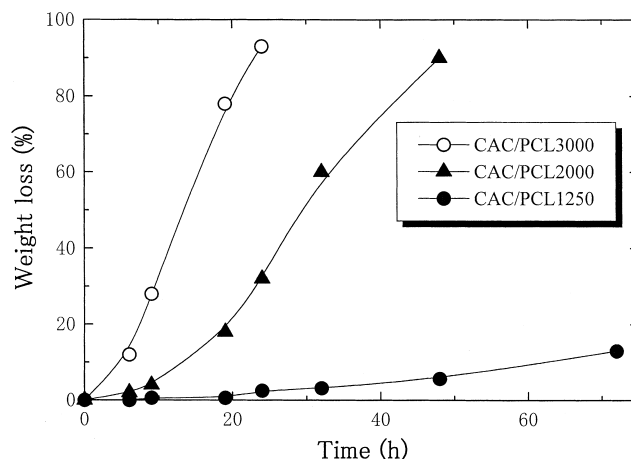

Fig. 6. Effect of molecular weight of PCL-diols on weight loss of various CAC/PCL films photocured for 90 min. (○) CAC/PCL3000; (▲) CAC/PCL2000; (●) CAC/PCL1250.

300% extension and showed the weight losses of 30–93% after 10 day incubation in the buffer solution with *Ps. cepacia* lipase, suggesting a good biodegradability. The photocured CAC/PCL1250 film is promising as a novel biodegradable elastomer for biomedical applications as well as environmental applications.

References

[1] For example, (a)Tokiwa Y. Sen-i Gakkaishi Jpn 1991;47:522. (b) Lenz RW. Adv Polym Sci 1993;107:22. (c) Mochizuki M. Sen-i Gakkaishi Jpn 1996;52:200. (d) Kaplan DL. Biopolymers from renewable resources. New York: Springer; 1998. p. 367.

[2] Nijenhus AJ, Grijpma DW, Pennings AJ. Polymer 1996;37:2783.

[3] Doytcheva M, Dotcheva D, Stamenova R, Orahovats A, Tsvetanov CH, Leder J. J Appl Polym Sci 1997;64:2299.

[4] Kim DJ, Kim WS, Lee DH, Min KE, Park LS, Jeon IR, Seo KH. J Appl Polym Sci 2001;81:1115.

[5] Vyavahare N, Kohn J. J Appl Polym Sci 1994;32:1271.

[6] Darwis D, Mitomo H, Enjoji T, Yoshi F. J Appl Polym Sci 1998;68: 581.

[7] Song CL, Yoshii F, Kume T. J Macromol Sci: Pure Appl Chem 2001; A38:961.

[8] Jin F, Hyon S-H, Iwata H, Tsutsumi S. Macromol Chem Rapid Commun 2002;23:909.

[9] Egerton PL, Trigg J, Hyde EM, Reiser A. Macromolecules 1981;14: 100.

[10] Nakayama Y, Matsuda T. J Polym Sci Polym Chem Ed 1992;30:2451.

[11] Matsuda T, Mizutani M. Macromolecules 2000;33:791.

[12] Matsuda T, Mizutani M, Arnold SC. Macromolecules 2000;33:795.

[13] Matsusaki M, Kishida A, Stainton N, Ansel CWG, Akashi M. J Appl Polym Sci 2001;82:2357.

[14] Nagata M, Hizakae S. Macromol Biosci 2003;3:412.

[15] Krigbaum WR, Kotek R, Ishikawa T, Hakemi H. Eur Polym J 1984; 20:225.

[16] Haddleton DM, Creed D, Griffin AC, Hoyle CE, Venkataram K. Macromol Chem Rapid Commun 1989;10:391.

[17] Khambutter FB, Warner F, Russel T, Stein RS. J Polym Sci Polym Phys Ed 1976;14:1391.

[18] Navarro F, Serrano JL. J Polym Sci Polym Chem Ed 1989;27:3691.

[19] Gan Z, Liang Q, Zhang J, Jing X. Polym Degrad Stab 1997;57:207.