

Synthesis and Properties of Graft Copolymer of Cellulose Diacetate with Poly(caprolactone monoacrylate)

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ABSTRACT: Cellulose diacetate grafting poly(caprolactone monoacrylate) copolymers (CDA-g-PCLA) were synthesized by a two-step reaction of cellulose diacetate (CDA) with poly(caprolactone monoacrylate) (PCLA). The isocyanate-terminated intermediate (NCOPCLA) was prepared and grafted onto cellulose diacetate chains. The results of the structure analysis indicated that PCLA was connected to CDA by chemical bonding. The flow temperature of graft

copolymers was lower than that of the pure CDA and decreased with increasing the grafting percentage. Outdoor soil burial tests and active sludge tests indicated that the graft copolymers have good biodegradability in natural conditions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 85–90, 2003

Key words: graft copolymers; biodegradable; synthesis

INTRODUCTION

In recent years, much attention has been given to the environmental pollution from nondegradable plastic wastes. As a biodegradable polymer, cellulose material is an attractive and economically feasible alternative material for developing degradable plastics.¹ A cellulose graft copolymer is an example of modification of the cellulose molecule by chemical derivation for use in thermoplastic production.^{2,3} Cellulose diacetate⁴ (CDA) is one of the most important cellulose esters. It was used widely in various fields, such as textile, membrane separation, plastics, filter material, film, paint, etc. However, this material has a high flow temperature (T_f), which results in problems of processibility compared with typical commercial plastics. Traditional plasticizations of CDA often result in bleeding of the plasticizers and the harmful characteristics or problems of the decomposition products.⁵ It is believed that the introduction of flexible segments by chemical bonding on the CDA backbone may improve the processibility of the CDA. In this article, novel graft copolymers were prepared by introducing flexible poly(caprolactone monoacrylate) (PCLA) chains onto the CDA backbone. The thermal and mechanical properties and biodegradability of the graft copolymers (CDA-g-PCLA) are discussed.

EXPERIMENTAL

Materials

Cellulose diacetate (CDA), supplied by Eastman Chemical Company, has a degree of substitution (DS) of 2.0 and a number molecular mass M_n of 7.8×10^4 . Toluene-2,4 diisocyanate (TDI) was supplied by Tokyo Chemical Industry Company. Dibutyltin dilaurate (DBTDL) was supplied by Fluka Company. Poly(caprolactone monoacrylate) (PCLA), with a molecular mass of 344, was supplied by Union Carbide Company. Other chemical reagents were analytically pure.

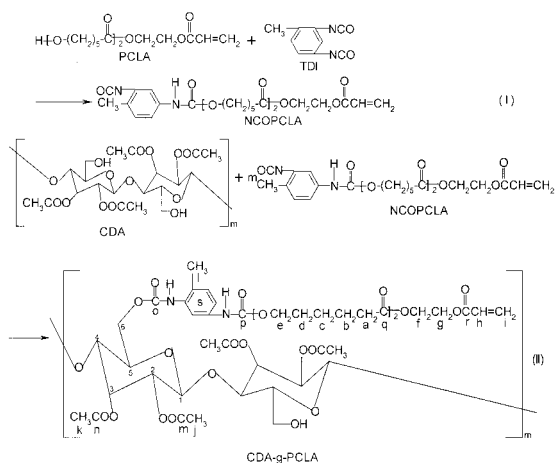
Preparation of end isocyanate intermediate NCOPCLA

TDI (1.74 g) and acetone (15 mL) were placed in a three-necked flask and mixed by stirring. Then, 3.44 g of PCLA and 15 mL of acetone were added at 60°C. The reaction began when 0.01 mL of catalyst DBTDL was added. The reaction was maintained for 3 h. The reaction product was coagulated in hexane, washed with pentane, and filtered. The white powder intermediate NCOPCLA (I) was obtained in almost quantitative yield (Scheme 1).

Preparation of CDA-g-PCLA

Intermediate NCOPCLA was added to a three-necked flask containing 12.30 g of CDA and 150 mL of acetone at 60°C. The reaction began when 0.01 mL of catalyst DBTDL was added and was maintained for 10 h. The reaction product was coagulated in ethanol and fil-

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Scheme 1 Reaction scheme of CDA-g-PCLA.

tered. Then, it was extracted in chloroform for 24 h to remove the residual raw materials and NCOPCLA. The product was dissolved in acetone and cast on a glass gasket, which settled for 12 h. The dried pure graft copolymer film was obtained after further drying under vacuum for 24 h (Scheme 1, compound II). The grafting percentage (%G) and weight percent of PCLA in graft copolymers (% W_{PCLA}) were calculated by the following equations:

$$\%G = (W_1 - W_0) \times 100 / W_0 \quad (1)$$

$$\%W_{\text{PCLA}} = (W_1 - W_0 - W_2) \times 100 / W_1 \quad (2)$$

where W_0 , W_1 , and W_2 are the weights of CDA, graft polymer, and TDI, respectively.

Characterization

Elemental analysis for carbon, hydrogen, and nitrogen was performed with an elemental analyzer (Model CHN-O-RAPID, Heraeus Company, Germany). The Fourier transform infrared (FTIR) spectra of the raw materials and the graft copolymers were measured with a spectrophotometer (RFX-65, Analect Company, USA), using KBr pellets in the range $400\text{--}4000\text{ cm}^{-1}$. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were obtained at 25°C with a spectrometer (DRX 400, Bruker, USA), using $\text{CO}(\text{CD}_3)_2$ as the solvent and trimethylsilane (TMS) as the internal standard.

The molecular mass of the graft copolymers was determined by gel permeation chromatography (GPC; Waters 551). Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1 mL/min, and polystyrene (PS) standards were used to obtain the universal calibration curve.

The thermal properties of the graft copolymers were determined with a differential scanning calorimeter (DSC; DSC-2C, Perkin-Elmer Company, USA) under nitrogen atmosphere at a rate of $10^\circ\text{C}/\text{min}$ from 50 to 300°C .

The mechanical properties of the graft copolymers were measured with a universal testing machine (AG-I, Shimadzu Company, Japan), according to ASTM D882, at a tensile speed of 50 mm/min.

X-ray diffraction (XRD) was measured with an X-ray diffractometer (D/max-1200, Rigaku Denki, Japan). XRD patterns with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \times 10^{-10}\text{ m}$) at 40 kV and 30 mA were recorded at $2\theta = 6\text{--}40^\circ$. The degree of crystallinity (χ_c) was calculated according to the usual method.⁶

The CDA and CDA-g-PCLA graft copolymers films were put into the soil and active sludge for degradation for different periods. Weight loss rate of the samples during the degradation in the soil burial and the active sludge was calculated according to the following formula:⁷

$$\text{Weight loss rate (\%)} = (G_0 - G_i) / G_0 \times 100$$

where G_0 is the weight of the sample before treatment, and G_i is the weight of the sample after treatment for i days.

Intrinsic viscosity $[\eta]$ of graft copolymers was measured with an Ubbelohde capillary viscometer in the THF solutions. The temperature was controlled at $30 \pm 0.02^\circ\text{C}$ during the measurement.

RESULTS AND DISCUSSION

Synthesis

In general, isocyanates can easily react with compounds containing active protons, such as alcohols, amines, and acids.^{8–10} The intermediate NCOPCLA produced as shown in Scheme 1 (I), contains a carbamate group and an —N=C=O , indicating that only one of two —N=C=O in TDI took part in the

TABLE I
Changes of —NCO and Amide II Band in FTIR Spectra with the Reaction Time

Absorbance	Step 1 Reaction Time (h)			Step 2 Reaction Time (h)			
	1	2	3	3	4	8	10
$A_{2273\text{cm}^{-1}}/A_{2950\text{cm}^{-1}}$	2.25	1.82	1.78	1.21	1.04	0.27	0
$A_{1538\text{cm}^{-1}}/A_{2950\text{cm}^{-1}}$	1.46	1.58	1.59	1.48	1.51	1.60	1.61

TABLE II
Relationship of Graft Copolymers and Reaction Conditions

Copolymer	PCLA (g)	TDI (g)	CDA (g)	C_{at} (mL)	G (%)	PCLA wt %
F0524	3.44	1.74	7.38	0.02	58.53	22.05
F0525	3.44	1.74	12.30	0.02	39.84	18.37
F0526	3.44	1.74	17.22	0.02	28.92	14.59
F0527	3.44	1.74	22.14	0.02	21.50	11.23

addition reaction. The unreacted $-\text{N}=\text{C}=\text{O}$ group in the intermediate can thus be used in further isocyanation with CDA. The reaction process was monitored by IR spectroscopy to determine the increasing absorption of carbamate group at 1538 cm^{-1} and the decreasing absorption of $-\text{N}=\text{C}=\text{O}$ at 2273 cm^{-1} , as shown in Table I. At the first step, the controlled isocyanation of TDI with PCLA was at an equal molar ratio. After 3 h, the reaction mass showed no more changes in IR absorption. These results indicated that intermediate NCOPCLA was formed. At the second step, $A_{2273\text{ cm}^{-1}}/A_{2950\text{ cm}^{-1}}$ decreased with increase of time and $A_{1538\text{ cm}^{-1}}/A_{2950\text{ cm}^{-1}}$ increased with increase of time. After 10 h, the IR absorbance of $-\text{N}=\text{C}=\text{O}$ in

the intermediate disappeared. This result indicated that the reaction was completed and CDA-g-PCLA was produced.

The grafting percentage G and the weight percent of PCLA in graft copolymers W_{PCLA} are shown in Table II. Decrease of the CDA usage is accompanied by an increase in G and an increase in W_{PCLA} in graft copolymers.

Structure characteristics

In Figure 1(a), the FTIR spectrum of the PCLA shows a strong hydroxyl peak at 3500 cm^{-1} and a sharp peak at 1732 cm^{-1} for the internal ester groups. In Figure 1(b), the CDA shows a typical broad hydroxyl peak at $\sim 3400\text{ cm}^{-1}$ on the Fourier transform infrared (FTIR) spectrum. By introducing NCO groups onto the PCLA

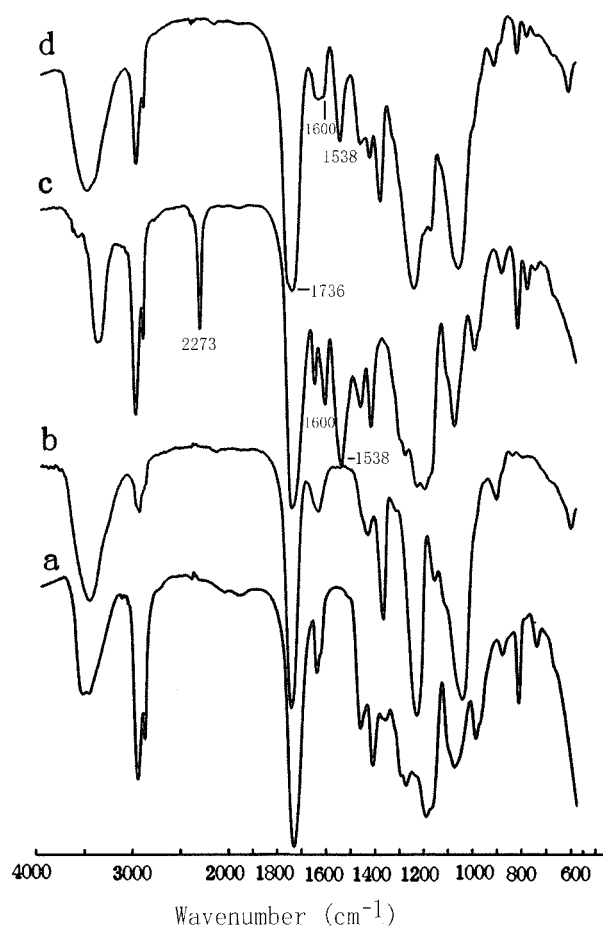


Figure 1 FTIR spectra of (a) PCLA, (b) CDA, (c) NCOPCLA, and (d) CDA-g-PCLA.

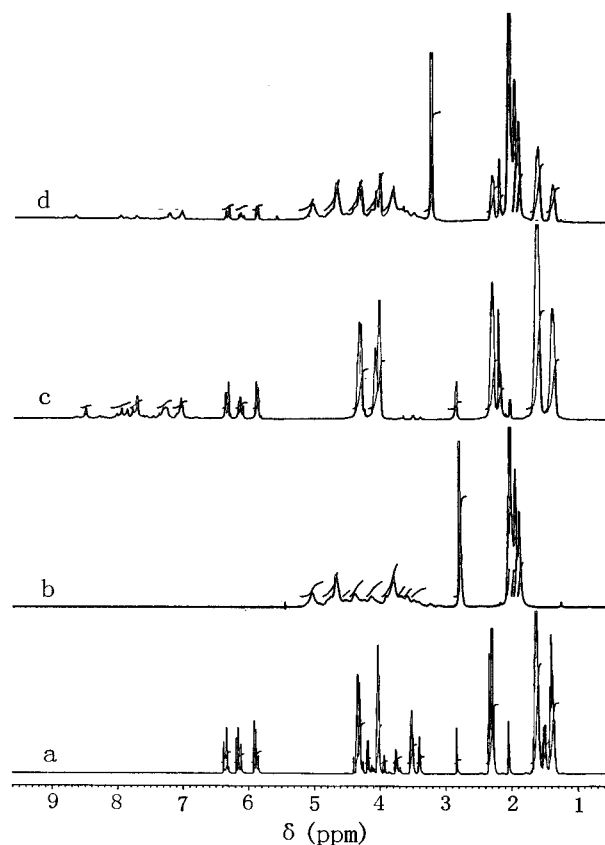


Figure 2 $^1\text{H-NMR}$ spectra of (a) PCLA, (b) CDA, (c) NCOPCLA, and (d) CDA-g-PCLA.

TABLE III
Molecular Mass and Crystallinity of Graft Copolymers

Copolymer	G (%)	M_n	M_w	M_w/M_n	X_c
F0524	58.53	118,928	218,717	1.84	0.34
F0525	39.84	101,812	195,821	1.92	0.28
F0526	28.92	95,096	180,317	1.90	0.31
F0527	21.50	85,606	164,359	1.92	0.29
CDA	0	78,194	191,109	2.44	Amorphous

terminal, the FTIR spectrum of NCOPLA [Fig. 1(c)] shows a new sharp peak at 2273 cm^{-1} representing the NCO groups and at 1538 cm^{-1} for the newly formed amide NH groups. The FTIR spectrum of NCOPLA shows a new peak at $\sim 1600\text{ cm}^{-1}$, which indicates the presence of the aromatic group originated from TDI. At the same time, the hydroxyl peak at $\sim 3500\text{ cm}^{-1}$ almost disappears in the NCOPCLA spectrum. By grafting NCOPCLA onto CDA, the FTIR spectrum of CDA-g-PCLA [Figure 1(d)] shows new peaks at 1736 cm^{-1} for the internal ester linkage, at 1538 cm^{-1} for the amide NH group, and at 1600 cm^{-1} for the aromatic ring from TDI. The NCO peak at 2273 cm^{-1} disappears in the CDA-g-PCLA spectrum, which means that the NCO group has changed to the carbamate group. The peak intensity of the hydroxyl groups in CDA is reduced by the substitution of NCOPCLA.

As shown in Figure 2(a), the proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) spectrum of PCLA shows a hydrocarbon around 1.38–2.32 and 4.01–4.35 ppm, methylene around 5.89–5.91 and 6.34–6.38 ppm, and hypomethylene around 6.12–6.19 ppm. The $^1\text{H-NMR}$ spectrum of NCOPCLA [Fig. 2(c)] shows new signals around 7.04–7.97 ppm, representing the aromatic hydrogen from TDI, and around 2.19 ppm, representing the methyl of TDI. The $^1\text{H-NMR}$ spectrum of CDA-g-PCLA [Fig. 2(d)] shows the peaks of CDA¹¹ [Fig. 2(b)], and the peaks of methylene and hypomethylene of PCLA.¹² The $^1\text{H-NMR}$ spectrum of CDA-g-PCLA also shows resonance at 2.19 ppm for the methyl of TDI, resonance at 7.05–8.01 ppm for the benzene ring, and resonance at 5.60 ppm for N–H. The $^1\text{H-NMR}$ spectrum confirms the grafting of NCOPCLA onto CDA.

The data in Table III indicate that both number-average molecular mass M_n and weight-average molecular mass M_w of graft copolymers increase with increasing G. The molecular mass distribution M_w/M_n , however, is decreased with increasing G. This result implies that when PCLA is grafted onto the CDA chains, both M_n and M_w of graft copolymers are larger than that of the pure CDA, but the molecular mass distributions becomes narrower than that of pure CDA.

According to the results in Table III, CDA is amorphous. The CDA-g-PCLA graft copolymer is semicrys-

talline, and its crystallinity is increased with increasing G because PCLA can be crystallized. When G is 21.5 and 28.9%, the crystallinity of the copolymers is 29 and 31%, respectively. This result implies that PCLA chains will promote the crystallization of the CDA chains when the PCLA chains are grafted on the CDA backbone.

Thermal properties

The data in Table IV indicate that the flow temperature decreases with an increase of G. This result means that after PCLA is grafted onto the CDA backbone, the interactions between the CDA molecular chains are weakened and the rigidity of CDA is reduced. Therefore, graft copolymers are more easily fluent than the pure CDA, which results in the improvement of processibility of graft copolymers. The results observed by the hot stage method are consistent with the results by DSC measurements (Figure 3).

Mechanical properties

From Table IV, it can be found that the tensile strength of the graft copolymers is lower than that of the pure

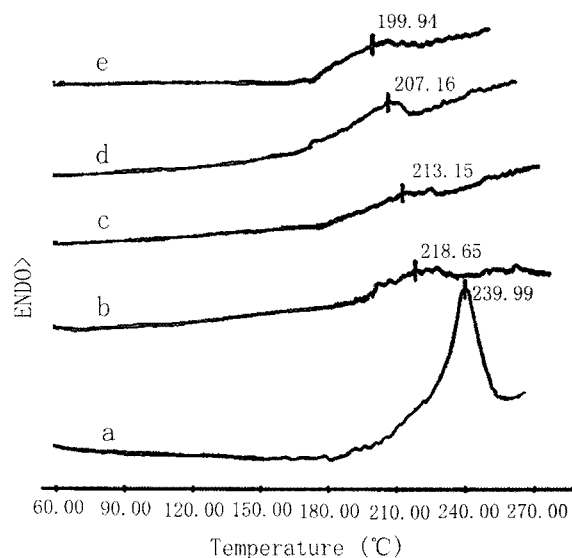


Figure 3 DSC curves of (a) CDA, (b) F0527, (c) F0526, (d) F0525, and (e) F0524.

TABLE IV
Mechanical and Thermal Properties of Graft Copolymers

Copolymer	G (%)	Tensile strength (MPa)	Elongation at break (%)	Flow temperature (°C)	T_m (°C)
F0524	58.53	34.00	25.6	203~205	199.94
F0525	39.84	39.28	17.5	208~210	207.16
F0526	28.92	44.01	15.0	214~216	213.15
F0527	21.50	47.42	13.1	218~220	218.65
CDA	0	49.25	11.3	245~250	239.99

CDA and is decreased with increasing G . This result implies that the interactions between the CDA molecular chains are weakened after PCLA is grafted onto the CDA backbone, and intermolecular hydrogen bonding is destroyed. But the elongation of the graft copolymers is larger than that of the pure CDA and is increased with increasing G . This result indicates that the flexible segments are introduced to CDA backbone after PCLA is grafted onto the CDA chains, and the tenacity of the graft copolymers is improved.

Biodegradable properties

The weight loss of the graft copolymers during the biodegradation in outdoor soil burial at 25–35°C is shown in Figure 4. These results indicate that both the CDA and graft copolymers show biodegradability in the natural soil condition. The weight loss of CDA is 10.60% and that of CDA-g-PCLA is 8.79% after 60 days. The weight loss of the graft copolymers during the biodegradation in active sludge at 25–35°C is shown in Figure 5. It can also be seen that CDA and graft copolymers exhibit good biodegradability. The weight loss of CDA is 30.12% and that of CDA-g-PCLA is 6.86% after 60 days. The biodegradability in active sludge is better than that in the natural soil condition. It might be expected that active sludge in-

clude more microorganisms, which have an important effect on CDA. However, when PCLA is grafted to CDA chains and side chains are formed, the biodegradability of the CDA is reduced.

The data of the intrinsic viscosity of CDA-g-PCLA copolymers before and after biodegradation in outdoor soil and active sludge are summarized in Table V. The intrinsic viscosity of CDA-g-PCLA is increased with biodegradation, ascends to the maximum after 30 days, and then decreases with further biodegradation. It is implied that the low molecular mass constituents are degraded preferentially in the initial stages, which results in the increase of the intrinsic viscosity of the remnant polymers. Also, the high molecular mass constituents begin to be degraded as degradation proceeds further, which results in the decrease of the intrinsic viscosity of the remnant polymers.

CONCLUSIONS

Graft copolymers of cellulose diacetate with poly(caprolactone monoacrylate) (CDA-g-PCLA) can be synthesized by a two-step method, and the reaction processes are monitored by FTIR. The structure of the graft copolymers is confirmed by FTIR, elemental analysis, GPC, and $^1\text{H-NMR}$. The tensile strength of the CDA-g-PCLA graft copolymers is decreased but the elongation is increased with increasing the graft

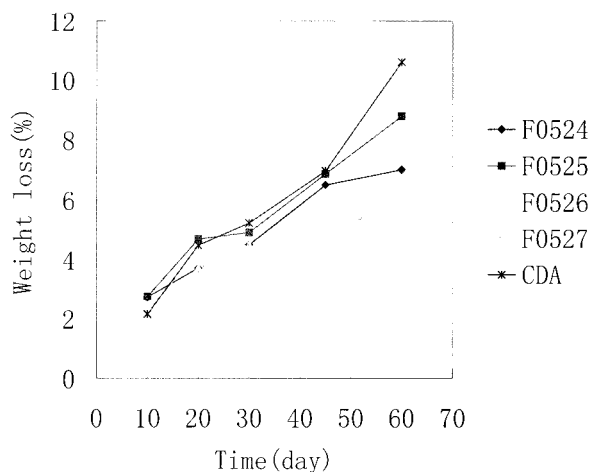


Figure 4 Weight loss of CDA and CDA-g-PCLA with time in outdoor soil burial.

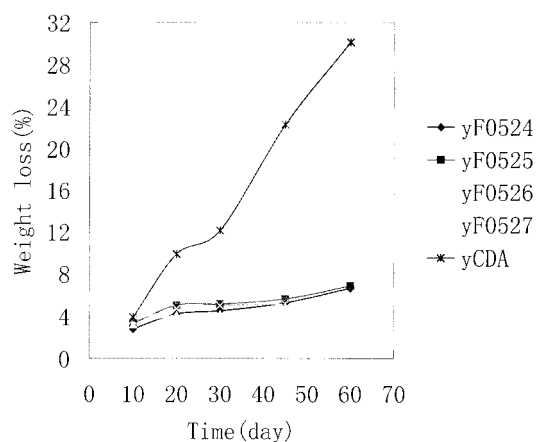


Figure 5 Weight loss of CDA and CDA-g-PCLA with time in active sludge.

TABLE V
Intrinsic Viscosity of Graft Copolymers Before and After Biodegradation in Outdoor Soil and Active Sludge

Sample	Condition	Intrinsic Viscosity (mL/g)					
		0 d	10 d	20 d	30 d	45 d	60 d
F0525	Soil	147.5	150.8	155.9	160.3	150.4	146.8
	Sludge	147.5	153.4	158.5	163.0	123.3	95.3
F0526	Soil	138.2	140.0	152.0	154.6	146.9	134.7
	Sludge	138.2	141.2	151.0	159.5	153.9	120.9
F0527	Soil	134.7	135.2	136.5	149.7	141.8	131.0
	Sludge	134.7	137.5	139.2	143.3	119.2	105.8

percentage G. The flow temperature of the graft copolymers is lower than that of the pure CDA. Outdoor soil burial tests and active sludge tests indicate that the graft copolymers have good biodegradability in natural conditions.

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