Partial Substitution of Cellulose by Ring-Opening Esterification of Cyclic Esters in a Homogeneous System

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ABSTRACT: Partially substituted cellulose derivatives were prepared by the regioselective derivatization of cellulose with cyclic esters (CEs), L-lactide (LA), and ε-caprolactone (CL), in a lithium chloride (LiCl)/*N*,*N*-dimethylacetamide solvent. They were characterized by spectroscopic analyses, calorimetry, solvent solubility inspection, and an enzymatic degradability test. Fourier transform Raman spectra of the cellulose derivatives confirmed that the CE moieties were covalently introduced into cellulose molecules at their hydroxyl groups via ring-opening esterification through the catalysis by LiCl. The ^{13}C-NMR analysis indicated that the ring-opened CEs were regioselectively combined with cellulose C6-OH. The CE portions were partially grafted on the cellulose backbone; the degree of substitution was ca. 0.5–0.7 and the degree of polymerization of grafted CEs was less than 3. Both cellulose derivatives were highly soluble in dimethylsulfoxide, which allows material fabrication. Some of the cellulose-LA was soluble or swollen in water, while cellulose-CL had poor affinity for water. Enzymatic degradation of cellulose-CEs occurred immediately on cellulase treatment, even under mild conditions which are not able to hydrolyze commercial cellulose diacetate at all. Some cellulose derivatives displayed endothermic changes. The cellulose derivatives prepared in this study are expected to be used as cellulose-based biomaterials with environmentally friendly features. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4358–4364, 2006

Key words: cellulose derivative; biodegradable cyclic ester; regioselective esterification; partial grafting; enzymatic degradation

INTRODUCTION

In recent years, biomass resources have attracted much public attention from an environmental perspective. Cellulose is the most abundant renewable biomass in the world, and has many useful applications. Cellulose consists of anhydroglucose (AHG) as a repeating unit, and has a linear and stereoregular structure through a β-1,4 glycosidic linkage. A variety of cellulose-based materials have been developed by utilizing the three hydroxyl groups per AHG unit that can be chemically modified by functional molecules.[1,2] Solvent solubility and plasticity are of great significance in the manufacture of industrial polymer products. However, cellulose is insoluble in common solvents, and has no thermoplasticity. Hence, functional design of cellulose has been carried out to improve the formability of the material for practical applications.

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Cellulose acetate (CA) is a typical cellulose derivative with high formability, and many CA products are being marketed: fibers, films, plastics, and industrial coatings. However, CA films with high degrees of substitution (DS) (approaching 3.0) show poor biodegradability.[3] Carboxymethylcellulose (CMC) is another typical cellulose derivative, and CMC with a low DS of around 0.5 is highly soluble in water and biodegradable, although water-soluble CMC has limited applications. Therefore, new biodegradable cellulose derivatives with good material formability are required for use as ecologically sound materials.

Polylactide (PLA) is a well-known biodegradable plastic material, which is produced from lactic acid obtained through the microbial transformation of biomass and its waste.[4] PLA products have material characteristics similar to those of conventional synthetic polymers, and can be used in practical applications. Furthermore, Teramoto and Nishio have reported practically beneficial performance of CA-*graft*-PLA (CA-*g*-PLA) derivatives prepared by the ring-opening reaction through residual hydroxyl groups of CA.[5,6] However, the biological degradation of CA and PLA in nature still needs to be further investigated. Highly substituted cellulose derivatives are highly resistant to biodegradation, especially enzymatic degradation. Our previous studies reported that commercial PLA products were quite difficult to degrade in natural

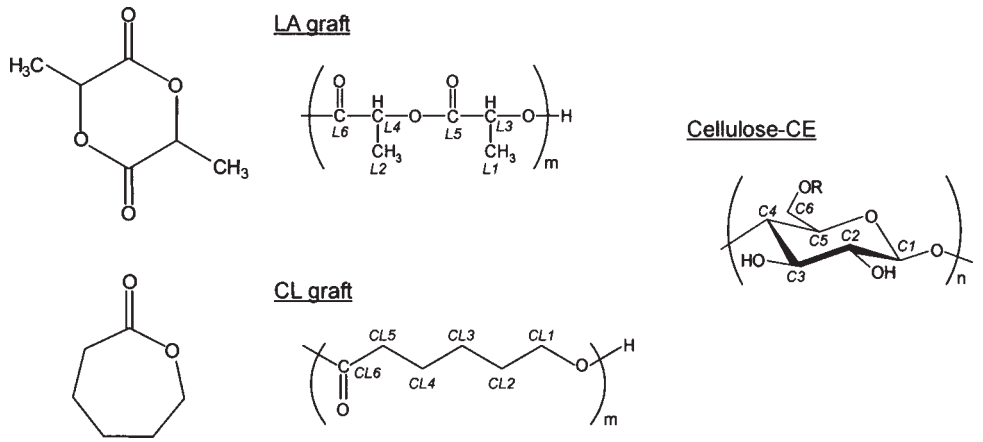

Figure 1 Chemical structures of L-lactide (upper) and ε-caprolactone (lower); possible structures of the cellulose-cyclic ester derivatives.

environments.[7–9] We also prepared paper-PLA composites with high biodegradability,[10] but further research was still required for cellulose/biodegradable polymer-related products.

In this study, cellulose derivatives were prepared by the homogeneous reaction of cellulose with two kinds of cyclic ester (CE), L-lactide (LA) and ε-caprolactone (CL), in a lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc) solvent system. CL is also a monomer of polycaprolactone, a commercial biodegradable plastic. Cellulose derivatives partially substituted with LA or CL moieties were characterized by Fourier transform (FT)-Raman and nuclear magnetic resonance (NMR) spectroscopies. Thermal properties, solvent solubility, and enzymatic degradability are also discussed.

EXPERIMENTAL

Materials

Whatman CF-1 cellulose powder (degree of polymerization (DP); ca. 200) was used as a starting material. Other chemicals, LA, CL, LiCl, DMAc, and tin(II) 2-ethylhexanoate were extra-pure reagent grade (Wako Pure Chemical Industries, Japan). The LA was dried *in vacuo* with phosphorus pentoxide for over 12 h before use, and other chemicals were used without further purification. Cellulase containing 1,4-β-D-glucan 4-glucanohydrolase (EC 3.2.1.4) and 1,4-β-D-glucan cellobiohydrolase (EC 3.2.1.91), which is produced by the fungus *Trichoderma viride*, was also purchased from Wako.

Dissolution of cellulose in LiCl/DMAc

Cellulose powders were pretreated by sequential solvent exchange through immersion in water (twice), acetone (twice), and DMAc (twice), in that order. Cellulose powders were suspended in the designated solvent for 2 h, and then freeze-dried after filtration at each step. The pretreated cellulose (0.40 g on dry weight) was added to LiCl (3.2 g)/DMAc (40 mL) solvent to make 1% (w/v) cellulose/8% (w/v) LiCl/DMAc solution, and the mixture was stirred at room temperature until it became clear.[11]

Ring-opening derivatization of cellulose

Cellulose/LiCl/DMAc solution (40 mL) was preheated at 128°C under a N_2 atmosphere. LA (1.4 g)/DMAc (40 mL) solution or liquid CL (1.1 mL)/DMAc (40 mL) (chemical structures shown in Fig. 1) were then added to the cellulose solution at a molar ratio of AHG/LA or AHG/CL = 1/4, and it was stirred at 128°C for 12 h under N_2. The reaction mixture was then gradually cooled down to room temperature and poured into pure acetone. The product isolated by centrifugation at 4800 × *g* for 10 min was purified three times with dimethylsulfoxide (DMSO) and acetone. After purification, the final product was washed with methanol, and dried *in vacuo* at room temperature for over 24 h. The reaction results are summarized in Table I.

Ring-opening grafting of cellulose

Either LA (2.8, 5.3, or 7.1 g)/DMAc (40 mL) solution or liquid CL (2.2, 4.1, or 5.5 mL)/DMAc (40 mL) (molar ratio of AHG/LA or AHG/CL was 1/8, 1/15, or 1/20, respectively) were added to the preheated 1.0% (w/v) cellulose/LiCl/DMAc solution containing tin(II) 2-ethylhexanoate (1.0 g) as a catalyst (molar ratio of AHG/catalyst was 1/1), and stirred at 128°C for 12 h in a N_2 atmosphere. The hydroxyl groups of cellulose were used as hydroxo-initiators of CEs in this system.[12] The reaction mixture was then gradually cooled down to room temperature, and poured into methanol/toluene (7/3 by volume). The products, cellulose-*g*-LA and cellulose-*g*-CL, isolated by centrifugation at 4800 × *g* for 10 min, were washed

TABLE I
Cellulose Derivative Sample Codes and Physical Properties

	Sample code	AHG/CE	Yield (%)	DS	DP_{CE}
Cellulose-LA	CLA1/4-0.6-2.1	1/4	42	0.6	2.1
Cellulose-CL	CCL1/4-0.7-1.8	1/4	44	0.7	1.8
Cellulose-*g*-LA	C*g*LA1/8-0.5-2.7	1/8	28	0.5	2.7
	C*g*LA1/15-0.6-2.5	1/15	16	0.6	2.5
	C*g*LA1/20-0.6-2.7	1/20	13	0.6	2.7
Cellulose-*g*-CL	C*g*CL1/8	1/8	31	ND	ND
	C*g*CL1/15	1/15	20	ND	ND
	C*g*CL1/20	1/20	17	ND	ND

ND: Not determined.

three times with methanol/toluene and with methanol, respectively. Cellulose-*g*-CL was insoluble in common solvents, and thus the purification was not sufficient. The final products were dried *in vacuo* at room temperature for over 24 h. The reaction results are summarized in Table I.

DP measurement

The DP values of the cellulose derivatives obtained were roughly estimated by the cupri-ethylenediamine method according to TAPPI Test Methods T230. DP values of cellulose powder treated in a similar manner but without LA and CL were also measured.

Solvent solubility inspection

Small portions (ca. 10 mg) of each sample (cellulose-CEs, cellulose and cellulose diacetate (CDA, DS ca. 2.4)) were poured into 1 mL of water or various organic solvents. After several hours at room temperature, the solvent solubility was approximately judged by visual inspection.

Enzymatic treatment

Cellulose and the derivatives were enzymatically treated with commercial cellulase. 25 mg samples (cellulose-CEs, cellulose, and CDA) and 2.5 mg of cellulase were added to 5 mL of acetate buffer (pH 5.0), and incubated at 37°C for 15 days. Enzymatic degradability was evaluated by an increase in the reducing sugar content using the 3,5-dinitrosalicylic acid (DNS) method,[13] where the degradability (%) was defined by dividing the amount of soluble sugar by the total amount of sample. All examinations were carried out at least three times.

Other analyses

FT-Raman spectra were recorded on a PerkinElmer System 2000 NIR FT-Raman spectrometer. The laser for excitation was a diode Nd:YAG at 1064 nm. All spectra were obtained in the 180° scattering geometry by using an InGaAs detector at a laser power of 300 mW and by averaging 400 scans with a resolution of 4 cm^{-1}. ^1H- and ^{13}C-NMR spectra were acquired at 37°C in DMSO-d_6 on a JEOL JMN-AL400 FT-NMR spectrometer (399.65 and 100.4 MHz, respectively). NMR spectra were analyzed using the accessory software equipped with the NMR apparatus; the DS and DP values were obtained by the equations indicated at the first subtitle section of Results and Discussion. X-ray diffractometry (XRD) was carried out using an X-ray diffractometer (XD-D1, Shimadzu, Japan) with Ni-filtered Cu Kα irradiation. Thermodynamic characteristics were estimated using a differential scanning calorimeter (DSC-50, Shimadzu, Japan) at a heating rate of 5°C/min from room temperature to 200°C under N_2, according to JIS K7121; the second run profiles were recorded.

RESULTS AND DISCUSSION

Characterization of cellulose-CEs

FT-Raman spectra of cellulose and its derivatives are shown in Figure 2. The characteristic Raman bands at

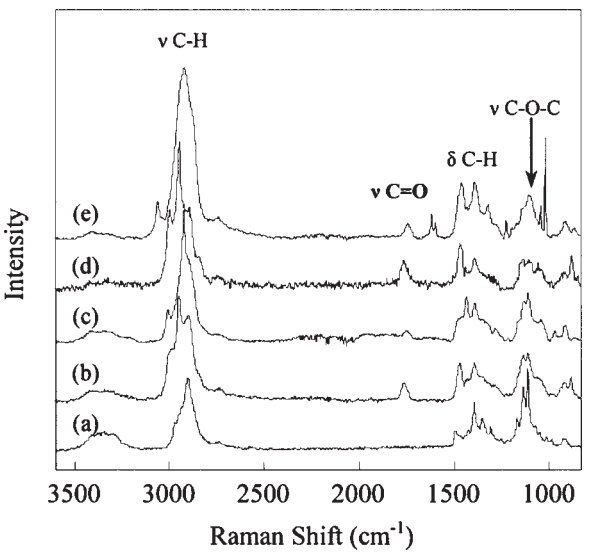

Figure 2 FT-Raman spectra of cellulose derivatives: (a) cellulose; (b) CLA1/4-0.6-2.1; (c) CCL1/4-0.7-1.8; (d) C*g*LA1/20-0.6-2.7; (e) C*g*CL1/20.

2900–2940 cm^{-1}, 1740 cm^{-1}, 1500–1200 cm^{-1} and 1090 cm^{-1} are assigned to the C—H stretching, C=O stretching, C—H bending, and glycosidic stretching frequencies, respectively. C—H stretching due to cellulose was observed at 2895 cm^{-1}, while clear peaks at 2942 and 2918 cm^{-1} appeared for cellulose-LA (CLA1/4-0.6-2.1, indicating a molar ratio of AHG/LA = 1/4, DS = 0.6 and DP of grafted LA = 2.1) and cellulose-CL (CCL1/4-0.7-1.8) (Table I), respectively. Additionally, the presence of a Raman band at 1740 cm^{-1}, corresponding to carbonyl groups, indicated that the ring-opened CEs were successfully introduced into cellulose-OH groups by esterification through on-site catalysis by LiCl.[14] Similar spectra were also observed with regard to cellulose-*g*-LA (C*g*LA1/20-0.6-2.7) and cellulose-*g*-CL (C*g*CL1/20) (Table I). The residual hydroxyl groups of cellulose were observed at 3100–3500 cm^{-1}, and gradually decreased with increasing CE derivatization.

^{13}C-NMR spectra of CLA1/4-0.6-2.1 are shown in Figure 3(a). The peaks at chemical shifts of 16.7, 20.4, 65.5, and 68.1 ppm were ascribed to L1, L2, L3, and L4 carbons (indexed in Fig. 1), respectively, of ring-opened LA portions. Carbonyl carbons from L5 and L6 appeared around 170 ppm. The peaks at 60.2, 80.2, 102.7, and 71.5–74.0 ppm were assigned to the C6, C4, C1 and C2, 3, 5 carbons of cellulose origin, respectively. Similarly, in the ^{13}C-NMR spectra of CCL1/4-0.7-1.8, the peaks at 24.9, 32.0, and 60.5 ppm were assigned to CL3/4, CL2/5, and CL1, respectively, [Fig. 3(b)]. The peak at 172.6 ppm was identified as the carbonyl carbon of CL6. In both spectra, the C6′ peak, which was due to the C6 carbons of LA- and CL-substituted hydroxyl groups of cellulose, appeared at around 63.1 and 63.4 ppm, respectively; ca. at a magnetic field 3 ppm lower than for the original C6. No other magnetic field shifts to lower values were observed, and thus the cellulose-C2 and C3 remained almost unchanged; i.e., the CE molecules did not combine at the C2 and C3 positions. A simple addition reaction of CEs to hydroxyl groups appears not to be novel, but such OH position-specific reaction may be an interesting fact. In this reaction system, the LiCl must be involved in both cellulose dissolution and ring-opening catalysis. Cellulose C3-OH has no relation to the formation of a cellulose/LiCl/DMAc complex due to the intramolecular hydrogen bond with the O5 of the adjacent AHG unit.[15] It has also been reported that the reactivity order for cellulose-OH is C2 > C6 ≫ C3 in heterogeneous systems, while C6 > C2 ≫ C3 in a LiCl/DMAc system.[16,17] Moreover, many researchers have reported that bulky moieties are regioselectively introduced at the C6-OH of cellulose.[18–20] Therefore, a preferential reaction with CEs at the cellulose C6 presumably occurred in this experimental system using bulk cellulose as a starting material, and the cellulose-CEs could have a comb-shaped architecture.

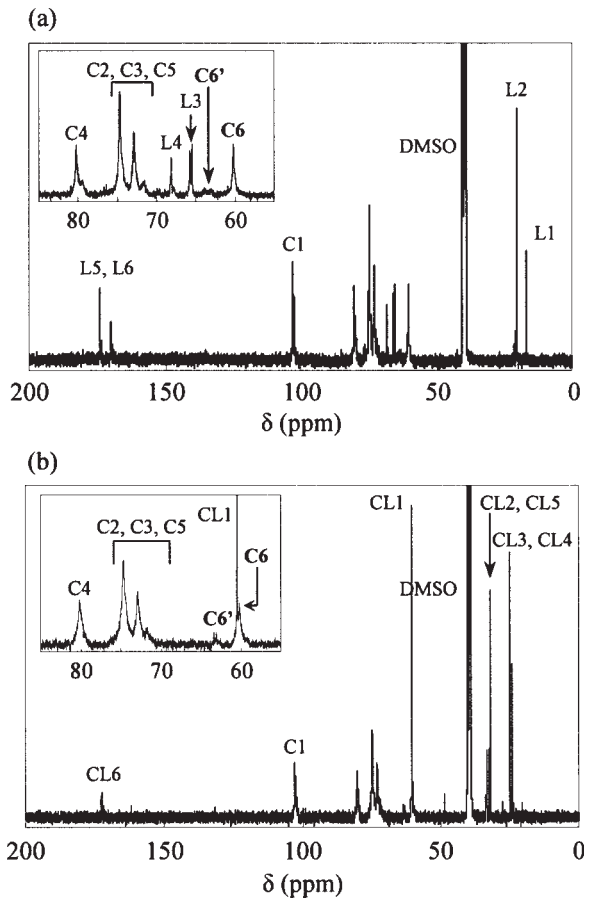

Figure 3 ^{13}C-NMR spectra of cellulose derivatives: (a) CLA1/4-0.6-2.1; (b) CCL1/4-0.7-1.8. Chemical shift assignments are indicated in Figure 1.

The DS values and the DP of the side chain (DP_{LA} and DP_{CL}), which are equal to the molar amounts of combined CEs per AHG unit of cellulose-CEs, were estimated directly by ^{1}H-NMR analysis of cellulose CEs in DMSO-d_6 according to the following equations:

$$DS = \frac{I_{H-C6'}}{I_{H-C6} + I_{H-C6'}} \quad (1)$$

$$DP_{LA} = \frac{I_{H-L1} + I_{H-L2}}{2I_{H-L1}} \quad (2)$$

$$DP_{CL} = \frac{I_{H-CL1} + I_{H-CL2} + I_{H-CL3} + I_{H-CL4} + I_{H-CL5}}{I_{H-CL1}} \quad (3)$$

where I_{H-C6} and $I_{H-C6'}$ are the peak areas of the C6 and C6′ protons, respectively, in the ^{1}H-NMR spectra (data not shown). In this case, further derivatization, e.g., peracetylation, could not be applied since some analytical problems occurred due to unknown side reaction, and thus sufficient accuracy was not ob-

TABLE II
Solvent Solubility of Cellulose and Its Derivatives

	Water	DMSO	DMF	DMAc	Acetone	Chloroform
Log P[a]	−	−1.30	−1.00	−0.17	−0.23	2.00
CLA1/4-0.6-2.1	++	+++	+++	−	−	−
CCL1/4-0.7-1.8	−	+++	+	−	−	−
Cellulose	−	−	−	−	−	−
Cellulose diacetate (DS 2.4)	−	+++	+++	+++	+++	+++

+++, soluble; ++, partially soluble; +, swollen; −, insoluble.
[a] Octanol–water partition coefficient.

tained through the rough resolution ^{1}H-NMR spectra. The DS values of CLA1/4-0.6-2.1 and CCL1/4-0.7-1.8 were ca. 0.6 and 0.7, respectively. The DS of the cellulose derivatives prepared at various molar ratios of AHG/CEs were almost constant, ranging from 0.5 to 0.7. The DP_{LA} and DP_{CL} values of derivatives were 2.1 and 1.8, regardless of the molar ratios of AHG/CEs. Increased CE addition had almost no effect on the direct esterification and polymerization of side chains. Theoretical DS at C6 position is 1 at maximum; however, bulky CE moieties were allowed not to be completely substituted due to steric hindrance. The DP_{LA} and DP_{CL} values were higher than 1, and thus the LA and CL molecules were slightly grafted at C6-OH on the cellulose backbone though catalyst-free addition reaction. However, the main structure of cellulose remained unchanged upon ring-opening esterification of CEs in the LiCl/DMAc solvent system.

Other properties of cellulose-CEs

The DP values of cellulose derivatives were assumed to be ca. 140 from the rough determination of CE-free cellulose which had been thermally treated at 128°C for 12 h under N_2. The original cellulose had a DP of ca. 200, and thus partial degradation of the cellulose chains occurred in this reaction system. All cellulose derivatives were amorphous, and had neither a glass transition point (T_g) nor a melting point (T_m), from the results of X-ray diffractometric and DSC analyses (data not shown). At this stage, bulky ring-opened substituents possibly inhibited the regular packing of cellulose derivative molecules.

Solvent solubility of cellulose-CEs

Table II lists the solubilities of cellulose derivatives in various solvents. CLA1/4-0.6-2.1 was soluble in DMSO and *N,N*-dimethylformamide (DMF). CCL1/4-0.7-1.8 showed high solubility in DMSO, and was swollen in DMF. Solubility in organic solvents is important for practical applications, e.g., preparation of fibers and films. Film formation by casting the cellulose-CE/DMSO solution on silicon wafer was possible. Cellulose should not be soluble in the solvents tested in this study, whereas cellulose diacetate, which has lower biodegradability than cellulose, was soluble in common organic solvents. Thus, the cellulose-CEs with low DS are expected to have both characteristics. It was suggested that the alkyl esters at cellulose C6-OH act as a solvation promoter for some organic solvents and as an inhibitor for the self-assembly of cellulose molecules. However, it is necessary to extend the side chain of CE molecules to improve polymer performance.

In addition, the CLA1/4-0.6-2.1 was partially soluble in water and a viscous suspension was obtained even though both cellulose and PLA are insoluble in water. Cellulose is inherently amphiphilic; however, the cellulose/cellulose interaction is stronger than water/cellulose and organic solvent/cellulose ones. The LA introduced at the cellulose C6-OH position effectively loosened the intermolecular attraction between cellulose molecules, and thus the amphipathic properties were enhanced. On the other hand, the CCL1/4-0.7-1.8 was insoluble in water and showed poor affinity for water, possibly because the CL molecule has a longer hydrophobic alkyl chain than the LA. Control of water accessibility for plastic materials is an important factor in biodegradation.

Enzymatic degradability of cellulose-CEs

Cellulase is ubiquitous in natural environments. Hence, enzymatic treatment with cellulase was carried out on cellulose and its derivatives as a model of a natural biodegradation system. Table III shows the enzymatic degradability of cellulosic samples without any thermal treatment. Both CLA1/4-0.6-2.1 and CCL1/4-0.7-1.8 were degraded more rapidly than the original cellulose by cellulase, but CDA, PLA, and PCL were not deteriorated at all under identical conditions. Cellulose-CL had a lower water affinity than cellulose-LA, but the enzymatic degradability of cellulose-CL was similar to that of cellulose-LA. These results might imply that the crystallinity has a large impact on the enzymatic degradability. Biodegradable polymers are easily degraded under composting conditions[21]; however, the degradation rates slow down remarkably in burial tests in soil.[7] Cellulase is a ubiquitous enzyme that plays an important role in the biodegradation of

TABLE III
Enzymatic Degradability of Cellulose and Its Derivatives by Cellulase Treatment

	Degradability (%)
CLA1/4-0.6-2.1	61.9
CCL1/4-0.7-1.8	67.2
Cellulose	17.2
Cellulose diacetate (DS 2.4)	0.7
Commercial PLA[a]	0.0
Commercial PLA[a]	0.0

[a] Evaluated by gravimetric analysis.

woody biomass, which is important for global carbon circulation. The cellulose-CEs with low DS values exhibit both solvent solubility and enzymatic degradability with cellulase, and are therefore expected to be practical, ecologically sound materials.

Properties and performances of cellulose-*g*-CEs

Cellulose-CEs exhibited good solvent solubilities and enzymatic degradabilities, but had poor thermal properties, and good thermal properties are very important for plastic products. Therefore, elongation of side chains was attempted to improve the performance of the cellulose-CEs. This was done by utilizing a tin catalyst for partial grafting of the CE portions. Table IV lists the properties and performances of cellulose-*g*-CEs. FT-Raman (in Fig. 2) and ^{13}C-NMR (data not shown) analyses showed that the LA and CL molecules were grafted only at the cellulose C6-OH, and presumably had a comb-shaped architecture. The DS and DP_{LA} of cellulose-*g*-LA, calculated by ^{1}H-NMR, were ca. 0.5–0.6 and ca. 2.5–2.7, respectively. Cellulose-*g*-LA was soluble in water and swollen in DMSO and DMF. On the other hand, cellulose-*g*-CL was not soluble in any of the solvents tested, and thus could not be subjected to ^{1}H- and ^{13}C-NMR analysis. Both cellulose-*g*-CEs were still amorphous, as shown by XRD analysis. The enzymatic degradability of both cellulose-*g*-CEs was greater than that of the original cellulose and that of common cellulose derivatives. Increasing the amount of CE addition brought about a gradual decrease in enzymatic degradability. However, sufficient degradability was retained up to a molar ratio of AHG/CE = 1/20 (C*g*LA1/20-0.6-2.7 and C*g*CL1/20).

TABLE IV
Solvent Solubility and Enzymatic Degradability of Cellulose-*g*-CEs

	Solubility			Degradability (%)
	Water	DMSO	DMF	
C*g*LA1/8-0.5-2.7	+++	+	+	63.3
C*g*LA1/15-0.6-2.5	++	+++	+	43.5
C*g*LA1/20-0.6-2.7	++	+++	+	33.5
C*g*CL1/8	−	−	−	57.8
C*g*CL1/15	−	−	−	43.2
C*g*CL1/20	−	−	−	34.4

+++, soluble; ++, partially soluble; +, swollen; −, insoluble.

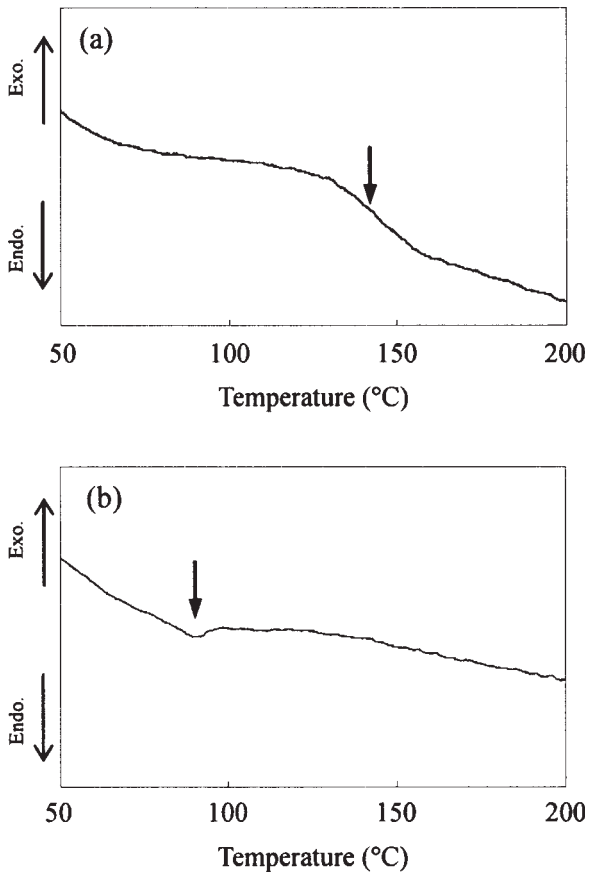

Figure 4 DSC profiles of (a) C*g*LA1/20-0.6-2.7 and (b) C*g*CL1/20.

Figure 4 shows the DSC profiles of cellulose-*g*-CEs. C*g*LA1/20-0.6-2.7 and C*g*CL1/20 had endothermic peaks at ca. 140°C and ca. 90°C, respectively. In general, PLA has a T_g at 66°C and a T_m at 177°C, and PCL has a T_g at −60°C and a T_m at 60°C. Cellulose has no such thermodynamic behavior before pyrolysis; however, the LA or CL molecules partially grafted on the cellulose backbones made a great contribution to the thermodynamic characteristics even though only small amounts of CEs were introduced into the cellulose. Positional selectivity and slight grafting of CEs provided us with further information on the modification of cellulose-based polymers. These results indicated that the selective grafting of cellulose with CEs in a homogeneous system may be effective for making an ecomaterial with significant performance that is lacking in typical synthetic polymers.

CONCLUSIONS

Novel cellulose derivatives that could be used as biodegradable, functional materials were successfully prepared with cyclic esters (L-lactide (LA) or ε-capro-

lactone (CL)) in a lithium chloride/dimethylacetamide solvent system. The ring-opened LA or CL moieties were selectively introduced at the C6-OH of cellulose molecules, resulting in a comb-shaped architecture. These cellulose derivatives with low degrees of substitution (around 0.5–0.7) were soluble in some organic solvents such as dimethylsulfoxide that make them available for material fabrication. They demonstrated thermodynamic characteristics on partial grafting of the oligoesters on the cellulose backbone, and could be rapidly degraded by enzymatic hydrolysis with commercial cellulase. Thus, the cellulose derivatives prepared in this study can be expected to be useful polymer materials with a diversity of applications in an environmentally friendly society.

References

1. Edgar, K. J.; Buchanan, C. M.; Debenham, J. S.; Rundquist, P. A.; Seiler, B. D.; Shelton, M. C.; Tindall, D. Prog Polym Sci 2001, 26, 1605.
2. Heinze, T.; Liebert, T. Prog Polym Sci 2001, 26, 1689.
3. Buchanan, C. M.; Gardner, R. M.; Komarek, R. J. J Appl Polym Sci 1993, 47, 1709.
4. Mohanty, A. K.; Misra, M.; Hinrichsen, G. Macromol Mat Eng 2000, 276, 1.
5. Teramoto, Y.; Nishio, Y. Polymer 2003, 44, 2701.
6. Teramoto, Y.; Nishio, Y. Biomacromolecules 2004, 5, 397.
7. Kanie, O.; Ishikawa, H.; Ohta, S.; Kitaoka, T.; Tanaka, H. J Fac Agr Kyushu Univ 2002, 47, 89.
8. Mayumi, A.; Kanie, O.; Kitaoka, T.; Wariishi, H.; Tanaka, H. J Fac Agr Kyushu Univ 2003, 48, 85.
9. Mayumi, A.; Kanie, O.; Kitaoka, T.; Wariishi, H.; Tanaka, H. J Fac Agr Kyushu Univ 2003, 48, 97.
10. Kanie, O.; Tanaka, H.; Mayumi, A.; Kitaoka T.; Wariishi H. J Appl Polym Sci 2005, 96, 861.
11. Dawsey, T. R.; McCormick, C. L. J Macromol Sci Rev Macromol Chem Phys 1990, 30, 405.
12. Kricheldorf, H. R.; Kreiser-Saunders, I.; Boettcher, C. Polymer 1995, 36, 1253.
13. Sengupta, S.; Jana, M. L.; Sengupta, D.; Naskar, A. K. Appl Microbiol Biotechnol 2000, 53, 732.
14. Ishizu, A.; Isogai, A.; Tomikawa, M.; Nakano, J Mokuzai Gakkaishi 1991, 37, 829.
15. Tosh, B.; Saikia, C. N.; Dass, N. N. Carbohydr Res 2000, 327, 345.
16. Miyamoto, T.; Sato, Y.; Shibata, T.; Inagaki, H.; Tanahashi, M. J. Polym Sci Polym Chem Ed 1984, 22, 2363.
17. Zhou, Q.; Zang, L.; Okamura, H.; Minoda, M.; Miyamoto, T. J Polym Sci A: Polym Chem 2001, 39, 376.
18. Stein, A.; Klemm, D. Makromol Chem Rapid Commun 1988, 9, 569.
19. Kondo, T.; Gray, D. G. Carbohydr Res 1991, 220, 173.
20. Nishimura, H.; Donkai, N.; Miyamoto, T. Cellulose 1997, 4, 89.
21. Puls, J.; Altaner, C.; Saake, B. Macromol Symp 2004, 208, 239.