

Effect of Dimethyl Sulfoxide on Synthesis of Thermoplastic Cellulose-Graft-Poly(L-lactide) Copolymer Using Ionic Liquid as Reaction Media

Sung Jun Lee,¹ Hae Sung Lee,¹ Sang Won Jeong,¹ Hyun-Chul Kim,¹ Se Geun Lee,¹ Tae Hwan Oh²

¹Nano & Bio Research Division, Daegu Gyeonbuk Institute of Science and Technology (DGIST), Daegu 711-873, South Korea

²Department of Nano, Medical and Polymer Materials, Yeungnam University, Gyeongsan 712-749, South Korea

Correspondence to: T. H. Oh (E-mail: taehwanoh@yu.ac.kr) and S. G. Lee (E-mail: sklee@dgist.ac.kr)

ABSTRACT: In this study, ring-opening graft polymerization of L-lactide onto cellulose was carried out homogeneously in ionic liquid (IL)/dimethyl sulfoxide (DMSO) co-solvent as a reaction media. Through the effective control of high viscosity and steric hindrance caused by the interaction between the IL and the hydroxyl group of cellulose by adding DMSO as a co-solvent, cellulose-graft-poly(L-lactide) (Cell-g-PLLA) copolymer with higher substitution efficiency was successfully prepared, at relatively low concentration of L-lactide. The maximum values of molar substitution, degree of lactyl substitution, and degree of polymerization of poly(L-lactide) in the copolymer were 3.76, 1.74, and 2.16, respectively, determined by ¹H-NMR. The prepared cell-g-PLLA copolymers showed thermal plasticization with a glass transition temperature of 155°C. In addition, the thermal processibility could be improved as the amount of grafted PLLA in the copolymer increased. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41331.

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INTRODUCTION

Cellulose is the most plentiful biopolymer on the Earth, and has various advantages such as low cost, biodegradability, excellent mechanical properties, and recyclability.^{1–4} However, because of a rather stiff rod-like conformation and numerous strong inter- and intra-molecular hydrogen bonds between the multiple hydroxyl groups of glucose units, cellulose is in water and most organic solvents. In addition, it is difficult to obtain thermally processible cellulose with intrinsic high crystallinity through extrusion or compression molding, which restricts its applications and cost-efficiency.

It has been reported that room-temperature ionic liquids (ILs) dissolve cellulose effectively.^{5–11} Among various ILs, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and 1-allyl-3-methylimidazolium chloride ([Amim]Cl) are known to be very effective in the dissolution of cellulose.^{8,9}

Recently, Zhao et al. and Xu et al. have investigated the solubility of cellulose in different ILs/polar solvents, and found that 1-butyl-3-methylimidazolium acetate ([Bmin]OAc)/dimethyl sulfoxide (DMSO) solvent showed the highest cellulose solubility owing to effect of DMSO on the cation–anion interactions of ILs.^{10,11} Also, Andanson et al. studied the role of co-solvents in ILs for dissolution of cellulose by using a synthetic phase

equilibrium method based on polarized microscopy and molecular simulation.¹² By the addition of DMSO to ILs, the viscosity of polymer solution dramatically decreased and the solvation capabilities of the IL was improved because of the facilitated mass transport without affecting the specific interactions between cations and anions or between IL and polymer.

To date, graft polymerization of cellulose in IL as a reaction media has been widely applied for better thermal processibility. Various polymers such as poly(*p*-dixanone), poly(*N*-isopropylacrylamide), and poly(L-lactide) have been grafted onto cellulose.^{13–16} A great deal of attention has been given to grafting biodegradable aliphatic polyesters onto cellulose. Dong et al. synthesized cellulose-graft-poly(L-lactide) (Cell-g-PLLA) copolymers by ring-opening graft polymerization of L-lactide onto cellulose in [Amim]Cl.¹⁶ However, the higher viscosity of IL and steric hindrance caused by the binding force between the IL and the hydroxyl group of cellulose has made it difficult to obtain Cell-g-PLLA with a higher molar substitution of L-lactide to enhance thermal processibility. In this study, IL/DMSO co-solvent system was investigated as a reaction media for the synthesis of Cell-g-PLLA to improve the substitution efficiency of PLLA. The molecular structures of the resulting copolymers were characterized by ¹H-NMR and wide angle X-ray diffraction (WAXD). The thermal properties were evaluated by thermogravimetric analysis

Table I. DS, MS, and DP_{PLLA} Values According to Reaction Conditions of Cell-g-PLLA Copolymers

Sample	Concentration of cellulose (wt %)	Cellulose/l-lactide (w/w)	DMSO/Ionic liquid (v/v)	Catalyst (wt %)	Temperature (°C)	Time (h)	DS	MS	DP _{PLLA}
Cell-g-PLLA 1	10	1/3	1/1	1	100	24	0.91	1.84	2.02
Cell-g-PLLA 2	10	1/4	1/1	1	100	24	1.08	2.24	2.07
Cell-g-PLLA 3	10	1/5	1/1	1	100	24	1.21	2.61	2.15
Cell-g-PLLA 4	10	1/6	1/1	1	100	24	1.16	2.41	2.08
Cell-g-PLLA 5	12	1/3	1/1	1	100	24	1.00	2.06	2.05
Cell-g-PLLA 6	14	1/3	1/1	1	100	24	1.17	2.42	2.07
Cell-g-PLLA 7	16	1/3	1/1	1	100	24	1.74	3.76	2.16
Cell-g-PLLA 8	10	1/5	1.5/1	1	100	24	1.55	3.66	2.35
Cell-g-PLLA 9	10	1/5	0.5/1	1	100	24	1.14	2.51	2.20
Cell-g-PLLA 10	10	1/5	0.25/1	1	100	24	1.12	2.47	2.20
Cell-g-PLLA 11	10	1/5	0/1	1	100	24	1.01	2.09	2.06
Cell-g-PLLA 12	10	1/5	2/1				Heterogeneous state		

(TGA), differential scanning calorimetry (DSC), and thermal molding test.

EXPERIMENTAL

Materials

Cellulose (Buck-eye, α -cellulose content > 95%) with a degree of polymerization of 850 was used. L-lactide (99.6%) was purchased from PURAC Biochem. [Bmin]Cl as ionic liquid with purity of a 99% was purchased from Aldrich Co. All products were dried in a vacuum at 70°C for 24 h before use. Stannous octanoate [Sn(Oct)₂] was distilled under vacuum and dissolved in freshly dried toluene. Other extra-pure grade reagents were used without further purification.

Preparation of Cell-g-PLLA Copolymers

Ring-opening graft polymerization conditions are summarized in Table I. Dry cellulose was dispersed into [Bmin]Cl with

stirring for 3 h at 100°C, to yield a clear solution. L-lactide and DMSO were added into the solution and the mixture was stirred at 90°C to give a homogeneous transparent solution. Sn(Oct)₂ was added and the reaction mixture was bubbled with N₂ for about 30 min. The reaction was carried out at 100°C in a N₂ atmosphere. The reaction mixture was then precipitated in ethanol to remove unreacted L-lactide, residual catalyst, and [Bmin]Cl. A mixture of Cell-g-PLLA and PLLA was obtained and dried for 24 h in vacuum. The polymer mixture was dispersed in dichloromethane and stirred for 72 h at room temperature to dissolve PLLA. After filtration, the product was washed several times with dichloromethane and then dried in a vacuum at room temperature for 24 h.

Characterization of Cell-g-PLLA Copolymers

¹H-NMR spectra of the synthesized Cell-g-PLLA copolymers were recorded on a Bruker 400 MHz spectrometer using

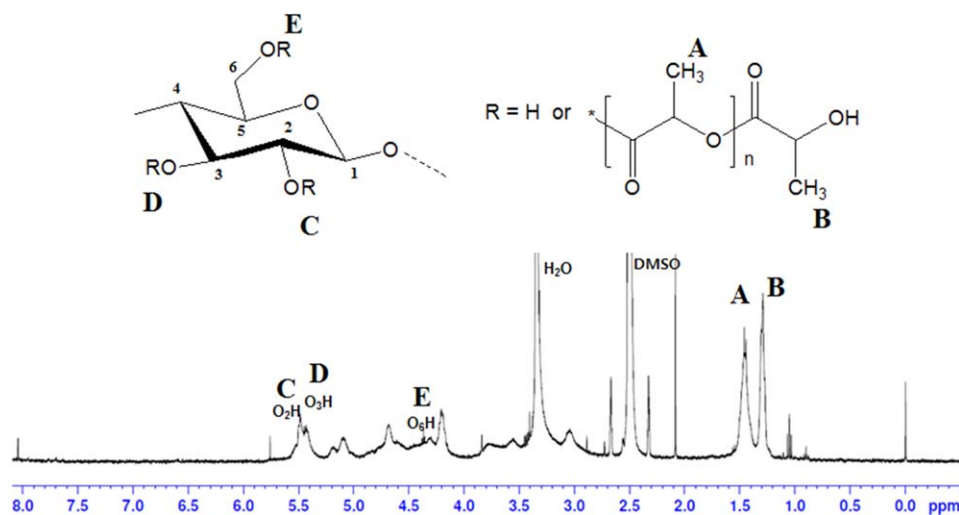


Figure 1. ¹H-NMR spectrum of cellulose-g-PLLA (MS = 3.76, DS = 1.74, DP_{PLLA} = 2.16). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

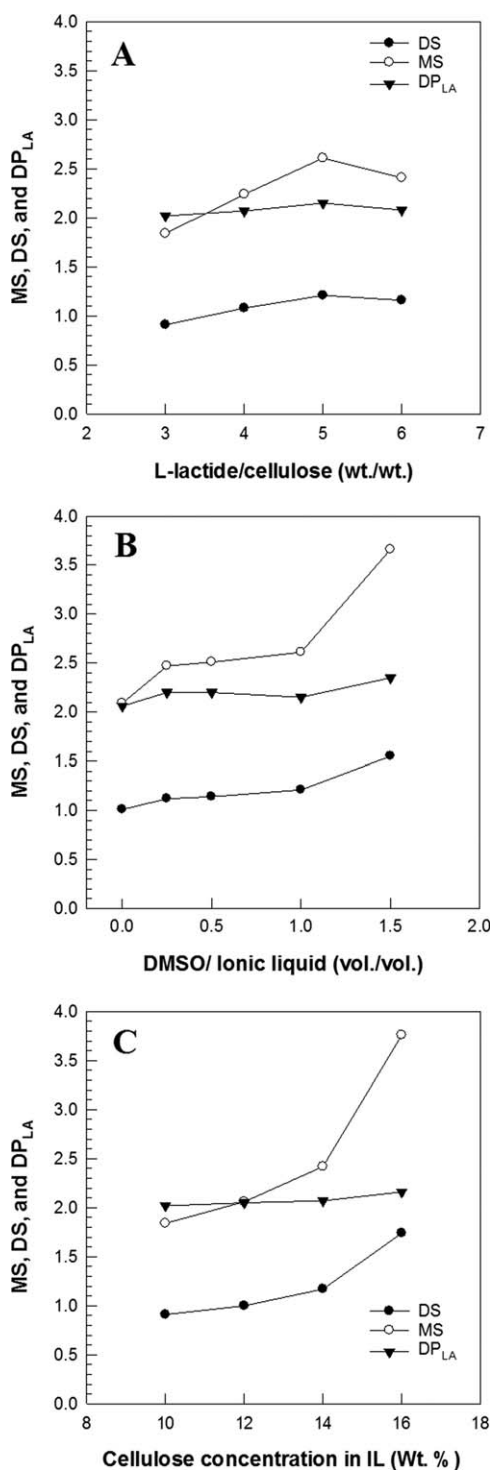


Figure 2. Variation in MS, DS, and DP of copolymer synthesized under various reaction conditions: (A) L-lactide/cellulose weight ratio, (B) DMSO/Ionic liquid volume ratio, and (C) cellulose concentration.

DMSO-d₆ as solvents. WAXD was performed using a Rigaku D/MAX-2500 X-ray diffractometer with Ni-filtered CuK radiation (40 kV, 100 mA) with 3°/min scanning rate at room temperature. TGA was conducted on a TA TG-DTA Q600 with a heating rate of 20°C/min from room temperature to 600°C in a nitrogen atmosphere. DSC was carried out on a DSC apparatus

(DSC Q200, TA) equipped with a cooler system. The samples were first heated from 20°C to 200°C at 20°C/min under a nitrogen gas flow to erase the previous thermal history before being rapidly cooled to 20°C. The samples were subsequently scanned at 50°C/min to observe the second heating scan. The DSC experiment was performed at a relatively high heating rate (50°C/min) to obtain a sharp glass transition temperature (T_g) because it was difficult to observe the T_g at a lower heating rate.

Thermal Molding Test of Cellulose-g-PLLA Copolymers

To confirm improved thermal processibility, the graft copolymer disks were prepared using a hot-press with a stainless steel plate (So Jung Measuring Instrument Company, Korea). The copolymer was placed between two plates and then heated to 180°C while pressing at constant pressure of 15 kgf/cm². The duration time for hot pressing was 5 min.

RESULTS AND DISCUSSION

The molar substitution (MS, an average number of introduced lactyl units per anhydroglucose of cellulose), degree of lactyl substitution (DS), and average degree of polymerization of the PLLA-side chain (DP_{PLLA}) of Cell-g-PLLA were estimated directly by ¹H-NMR analysis according to the equations proposed by Dong et al.¹⁶

$$\text{MS} = \frac{\text{Lactyl units}}{\text{Anhydroglucose units}} = \frac{\{(A+B)/3\}}{\{(C+D+E)/3\}} \quad (1)$$

$$\text{DS} = \frac{\text{Terminal lactyl units}}{\text{Anhydroglucose units}} = \frac{(B/3)}{\{(C+D+E)/3\}} \quad (2)$$

$$\text{DP}_{\text{PLLA}} = \text{MS}/\text{DS} = (A/B) + 1 \quad (3)$$

where lactyl units are the integral areas of the protons of lactyl -CH₃ (A) and terminal lactyl -CH₃ (B), respectively, and anhydroglucose units are the integral area of protons of residual hydroxyl [(three hydroxyl groups at C2 (C), C3 (D), and C6 (E))] in cellulose.

Figure 1 shows a ¹H-NMR spectrum for Cell-g-PLLA copolymer. MS, DS, and DP_{PLLA} values of synthesized copolymers were summarized in Table I.

Figure 2(A) shows the changes in DS, MS, and DP_{PLLA} according to the amount L-lactide against cellulose by fixing the cellulose concentration for IL, and the amount of DMSO against IL. The grafting content of PLLA in copolymers was increased as the in-feed ratio of monomer to cellulose was increased. However, DS of copolymers was decreased slightly at higher L-lactide concentration. The low substitution efficiency may be caused by the slightly reduced solubility of cellulose in IL/DMSO mixture at high concentration of L-lactide. Okaya et al. reported that the range of homogeneous phase in phase diagram of solvent mixture became narrower because of the presence of other material.¹⁷ Figure 2(B) shows the MS, DS, and DP_{PLLA} of cellulose depending on the addition of DMSO to ionic liquid. Up to 1/1 (v/v) of DMSO and IL, MS, DS, and DP_{PLLA} values increased slightly, but a big increase was observed over 1/1 (v/v). At a high DMSO content [e.g. 2/1 (v/v) in Table I], phase separation was dominant owing to the decreased solubility of cellulose. As shown in Figure 2(C), an increase in the cellulose concentration

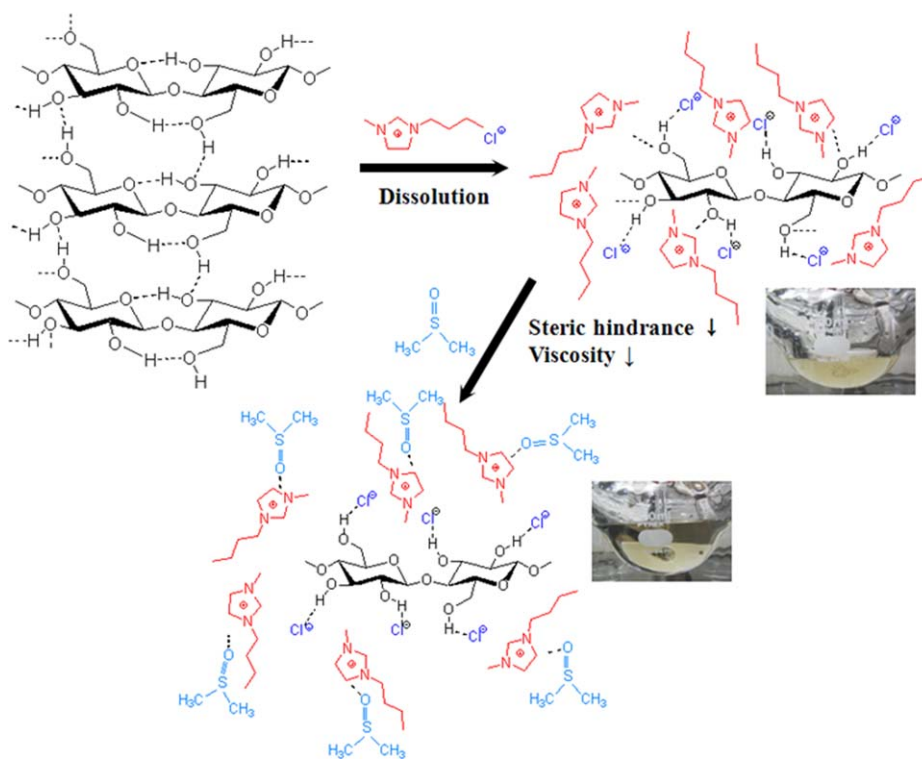


Figure 3. Schematic of interaction between IL and DMSO in cellulose solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

significantly increased grafting yield and induced a slight increase in DP_{PLLA} . This higher grafting efficiency might be explained by an increase in the reaction sites because of the increased polymer concentration. At concentrations greater than 16 wt %, the cellulose solution was not completely dissolved, implying that the solution was in a heterogeneous state, which was a disadvantage to polymerization.

Cell-g-PLLA copolymers have been prepared in different reaction conditions. In a *N,N*-dimethylacetamide/lithium chloride solvent, cellulose with DP of 200 showed DS of 0.5 when the cellulose concentration of 10 wt % and the molar ratio of cellulose to *L*-lactide of 1/8 (w/w) were employed.¹⁸ DS of 0.97 was reported in [Amin]Cl by using cellulose with DP of 600 at the cellulose concentration of 16 wt % and the weight ratio of cellulose to *L*-lactide of 1/2 (w/w).¹⁶ With high molecular weight cellulose (DP = 850), a homogeneous solution of up to 16 wt % could be prepared in IL/DMSO (1/1 (v/v)) and the highest of DS of 1.74 could be achieved when the weight ratio of cellulose to *L*-lactide was 1/3 (w/w). It has been suggested that during dissolution of cellulose in IL, the Cl anions and imidazolium cations interact with the protons and the oxygen of the cellulose hydroxyl groups, respectively, resulting in reduced hydrogen bonds between the cellulose chains.^{19,20} Accordingly, the strong binding force with cellulose molecular chains and relatively large cations caused by dissolution of the cellulose hinders the grafting reaction. Zhao et al.¹⁰ studied the effects of DMSO as a co-solvent on cellulose dissolution in [Bmin]OAc as IL and found that DMSO enhanced the solubility of cellulose in IL. The proposed dissolution mechanism is

similar to the interaction structure of each molecule in our reaction system. Figure 3 shows a schematic of molecular structures of each molecule indicating a role of DMSO in cellulose/IL solution. It is suggested that the interactive force of the imidazolium cation and DMSO weakens the interaction of the cellulose hydroxyl group and IL, resulting in the reduction of the steric hindrance caused by large cations in cellulose solution, and high substitution.

The crystalline state of copolymers, PLLA, and cellulose according to X-ray diffraction analysis was shown in Figure 4. PLLA revealed the strongest diffraction peak at $2\theta = 16.76^\circ$ and three diffraction peaks at $2\theta = 14.99^\circ$, 19.22° , and 22.56° . Cellulose displayed the diffraction peaks at $2\theta = 22.4^\circ$ and 16.5° merged into a broad band, which are in good agreement with the previous works.^{21–23} According to many researchers, after deconvolution, five bands were observed: the $2\theta = 15^\circ$ reflection assigned to (1 0 1) crystallographic plane, the $2\theta = 16.5^\circ$ to (1 0 $\bar{1}$), the $2\theta = 18.9^\circ$ to amorphous phase, and the $2\theta = 20.4^\circ$ to (0 0 2) or (2 0 0) plane of cellulose I. In the copolymer diffraction patterns, a broad diffused diffraction peak at around 2θ of 19° indicates an amorphous structure of the copolymer. These results suggest that the ordered structure of cellulose disappeared by graft polymerization of PLLA. Our X-ray diffraction data are consistent with the Cell-g-PLLA prepared in IL with organic catalyst.¹³

To investigate the thermal properties of the synthesized copolymers, TGA and DSC measurements were performed (Table II, Figures 5 and 6). As shown in Table II, measuring the residue

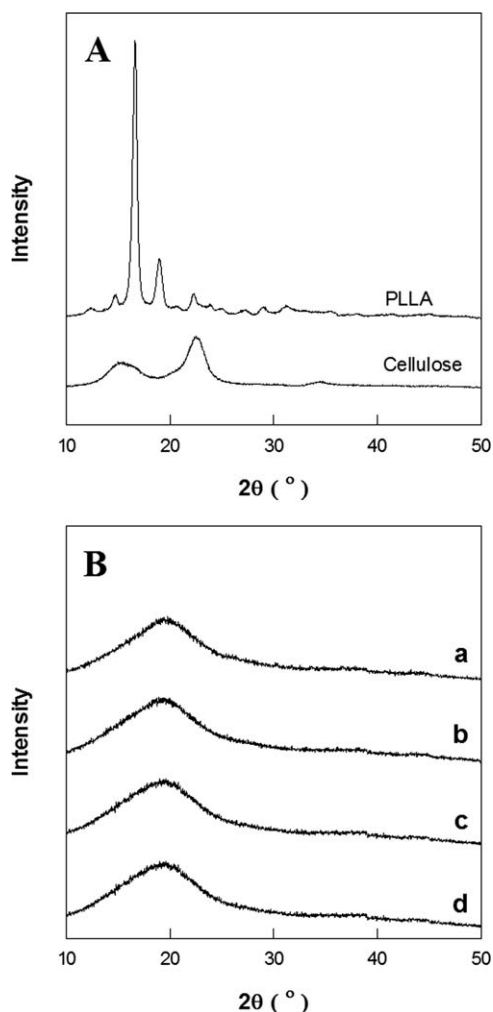


Figure 4. WAXD profiles of the (A) cellulose and PLLA and (B) copolymers with different DS: a, DS = 0.91; b, DS = 1.08; c, DS = 1.16; d, DS = 1.74.

of the final materials at off-set decomposition temperature upon TGA analysis enabled the grafting yield of PLLA introduced to the cellulose chain to be confirmed. This was because cellulose exists as a residue in the ash state at the time decomposition ends, and PLLA completely decomposes, leaving no residue. As might be imagined, the final residue at the off-set

Table II. Thermal Properties of Cell-g-PLLA Copolymers

Sample	DS	T_g (°C)	$T_{d1[onset]}$ (°C)	$T_{d2[onset]}$ (°C)	Residue (%)
Cellulose	-	-	244	-	13
PLLA	-	-	262	-	0
Cell-g-PLLA 1	0.91	-	217	-	16
Cell-g-PLLA 2	1.08	-	226	-	12
Cell-g-PLLA 4	1.16	160	226	303	10
Cell-g-PLLA 8	1.55	158	217	298	8
Cell-g-PLLA 7	1.74	155	213	290	8

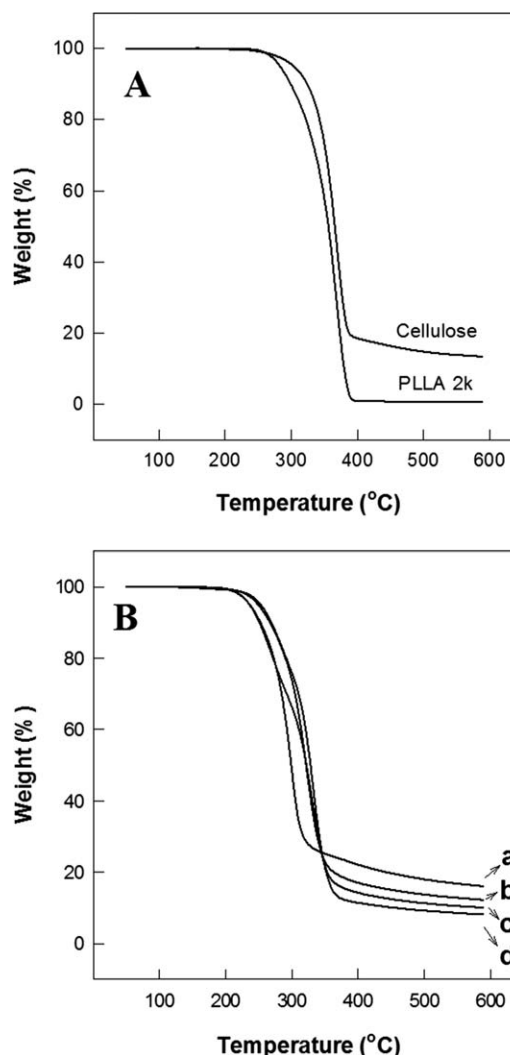


Figure 5. TGA thermograms of the (A) cellulose and PLLA and (B) copolymers with different DS: a, DS = 0.91; b, DS = 1.08; c, DS = 1.16; d, DS = 1.74.

decomposition temperature decreased as the DS of the copolymer increased.

The thermal degradation behavior of copolymers with DS values of 1 or higher showed two separate pyrolyses over the range of temperature examined (Figure 5). This is thought to be a result of the reaction activity of three hydroxyl groups at C2, C3, and C6, which is the cellulose chain. The three hydroxyl groups at the C2, C3, and C6 positions exhibited different reaction activities. Wu et al. and Takaragi et al. reported that the order of reactivity during cellulose acetylation in ionic liquid is C6-OH > C3-OH > C2-OH, which is similar to that observed in DMAc/LiCl.^{24,25} In the case of partially substituted cellulose acetate prepared by commercial methods, there are more free hydroxyls at C6 than at C2 and C3.²⁶ The hydroxyl group at C6 is the most reactive, while those of C2 and C3 are similar. Thus, when substitution of the hydroxyl group at C6 is almost complete, the substitution reaction of the hydroxyl group at C2/C3 commences. Accordingly, when the substitution occurs at the

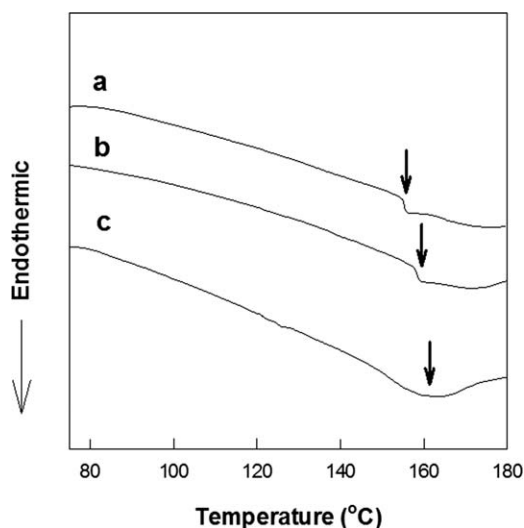


Figure 6. DSC thermograms of copolymers with different DS: a, DS = 1.74; b, DS = 1.55; c, DS = 1.16.

hydroxyl groups of C2/C3 which form a relatively stronger hydrogen bond than C6, it can be predicted that the thermal properties of the copolymer would dramatically change and the decomposition behavior of cellulose and PLLA would occur at the same time.

Figure 6 shows the DSC diagram of synthesized copolymers with different DS. Cellulose cannot be measured for glass transition temperature (T_g), which represents the mobility of the molecular chain because of the strong hydrogen bonding between the chain molecules and the stiffness of the chains themselves. These characteristics also make it difficult to measure T_g of commercial cellulose derivatives such as cellulose acetate and cellulose propionate. Teramoto et al. reported that the T_g of cellulose acetate with relatively higher DS (DS = 2.15) was

202°C using rapid quenching method.²⁷ The synthesized copolymers in this experiment showed T_g of about 155°C when the degree of substitution was greater than 1. This indicates that the hydrogen bonding of the hydroxyl groups of cellulose was effectively blocked by the substituent, which improved the mobility of the molecular chain.

Figure 7 shows cellulose and copolymer disks prepared using the hot press device. The cellulose had no thermo formability, and exhibited compression pack effect accompanied by a little bit of carbonization. In contrast, the synthesized copolymer could be formed into disk corresponding to fusible form. The thermo formability of the disk varied depending on the DS value of the copolymer. The disks exhibited less thermal denaturalization and improved transparency as DS increased,^{13,27} and noticeable thermal denaturalization occurring as DS decreased. This effect is caused by the increase in heat mobility of the cellulose, which was limited by strong hydrogen bonds as the degree of substitution increased.

CONCLUSIONS

In this experiment, the binding force of IL and cellulose hydroxyl was weakened via the coherence of DMSO and IL by adding DMSO co-solvent to the IL in which cellulose is dissolved. This resulted in increased substitution efficiency of PLLA and stabilization of the viscosity of the reaction system at high polymer concentration, which effectively controlled the reactivity. The prepared Cell-g-PLLA showed thermal plasticization with a glass transition temperature of 155°C. Moreover, through improvements in its thermal processing ability, the prepared Cell-g-PLLA can be applied to various high value-added fields of medical biodegradable plastic, film, and textile. The average molecular weight of cellulose, DS, and degree of polymerization of the grafted side chain can be controlled for development of the respective characteristics to fit suitable uses.

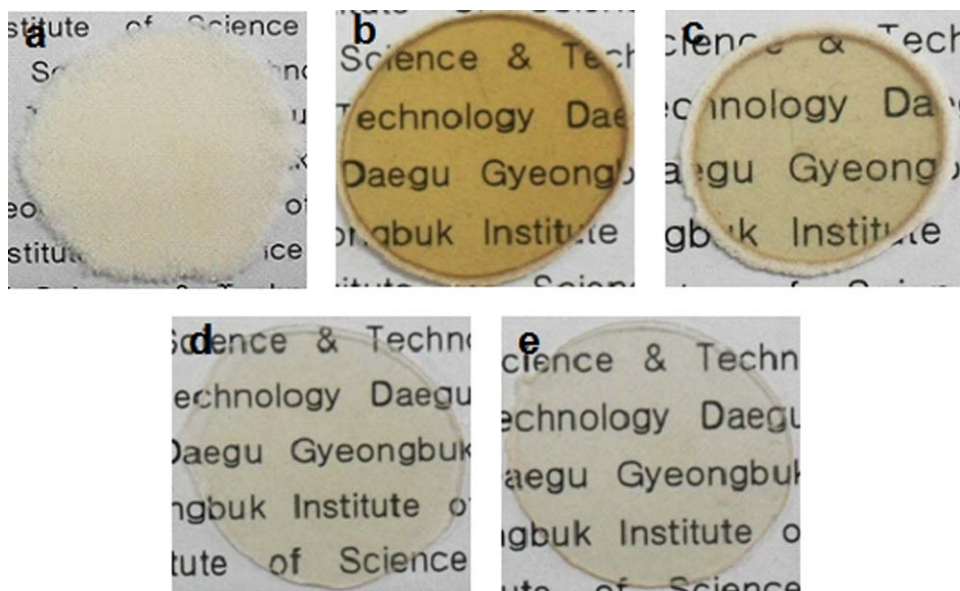


Figure 7. Photographs of cellulose and copolymer disks prepared using a hot press: a, cellulose; b, DS = 0.91; c, DS = 1.08; d, DS = 1.16; e, DS = 1.55. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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