

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.

For more information visit www.intechopen.com



Ionic Liquid as Green Solvent for Ring-Opening Graft Polymerization of ϵ -Caprolactone onto Hemicelluloses

X.Q. Zhang, M.J. Chen, H.H. Wang, X.X. Wen,
C.F. Liu and R.C. Sun

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/59679>

1. Introduction

The depletion of fossil fuels has led to rapidly increasing interest in the utilization of environmentally friendly, readily available, biodegradable, and renewable biomass to produce biofuels, biocomposites, biochemicals, and a host of other bioproducts [1-3]. Agricultural crop residues, such as cereal straws and sugarcane bagasse (SCB), are underutilized lignocellulosic biomass and have great potential for the production of biocompatible and biodegradable materials to replace fossil-based products [4,5].

Hemicelluloses, the second most abundant class of renewable and biodegradable polysaccharides found in nature after cellulose, account for on average about 20-35% of most plant materials [6,7]. Compared with cellulose and lignin, the exploiting of hemicelluloses was paid little attention until the last decades due to their inherent low molecular weight and heterogeneous structure. In their natural state, hemicelluloses are generally considered to be non-crystalline, with a DP of 80 to 200. They are heterogeneous polymers of pentose (xylose, arabinose), hexoses (mannose, glucose, and galactose), and sugar acids. Xylans are the most abundant hemicelluloses [8]. In many plant materials, xylans are heteropolysaccharides with homopolymeric backbone chains of 1,4-linked β -D-xylopyranose (Xylp) units [9]. In addition, there can be *O*-acetyl, α -L-arabinofuranosyl, α -1,2-linked glucuronic, or 4-*O*-methylglucuronic acid substituents on the backbone [10].

Chemical modification is an important way to impart biomass with desired properties for specific applications [11-13]. From the chemist point of view, a broad variety of chemical modification reactions both at OH groups and the C atoms are possible [14]. Ring-opening graft polymerization (ROGP) is a multifunctional modification technique for the synthesis of

polymers from cyclic monomers that can endow polymers with controlled molecular weights and molecular weight distributions [15-17]. Due to their excellent biodegradability, biocompatibility, and permeability, considerable attention has been paid to aliphatic polyesters from lactones and lactides, among which poly (ϵ -caprolactone) (PCL) is especially interesting for its applications [1,18,19]. It is a hydrophobic aliphatic polyester with excellent biocompatibility, low immunogenicity, nontoxicity, and good mechanical and thermoplastic properties, making it a potential matrix candidate in biocomposites [1,20,21]. Much consideration had been paid to graft copolymerization between cellulose derivatives and aliphatic polyesters [1,22,23]. In contrast to cellulose, there is a little information about the graft polymerization of biodegradable aliphatic polyesters onto hemicellulose. Moreover, reactions on hemicellulose are not easy, mainly because of the almost impossible proposition of dissolving hemicellulose in a suitable solvent without significant degradation.

In recent years, with the development of green chemistry and the requirement for environment protection, much attention has been focused on the utilization of ionic liquids as novel solvents and reaction media due to their eco-friendliness, negligible vapor pressure, non-flammability, chemical stability, good thermal stability, and high reaction rates [24]. In general, ionic liquids are screened with a range of anions, from small hydrogen-bond acceptors (Cl^-) to large noncoordinating anions, including Br^- , SCN^- , $[\text{PF}_6]^-$, and $[\text{BF}_4]^-$ [25]. They are capable of dissolving complex polymeric materials and macromolecules, such as carbohydrates. The ionic liquids can break the extensive hydrogen-bonding network in the polysaccharides and promote their dissolution [26]. Various polysaccharide derivatives have been prepared in ionic liquids from cellulose [27,28], hemicelluloses [11,26] and starch [29]. These results indicated that there are no derivatization reactions occur during the dissolution of polysaccharides in ionic liquids. They are satisfactorily homogeneous media [30], and can be desirable alternatives to conventional solvents and reaction media in modification.

The aim of the present research was to investigate homogeneous ROGP of ϵ -CL onto hemicelluloses using 1-butyl-3-methylimidazolium chloride ($[\text{C}_4\text{mim}]\text{Cl}$) ionic liquid as a homogeneous reaction medium with 4-dimethylaminopyridine (DMAP) as a catalyst to prepare hemicellulose-*g*-PCL copolymers. The physico-chemical properties of the graft copolymers were characterized by FT-IR, ^1H -NMR, ^1H - ^1H Correlation Spectroscopy (COSY), ^{13}C -NMR, ^1H - ^{13}C Correlation 2D NMR (HSQC), XRD, SEM and thermal analysis.

2. Experimental

2.1. Materials

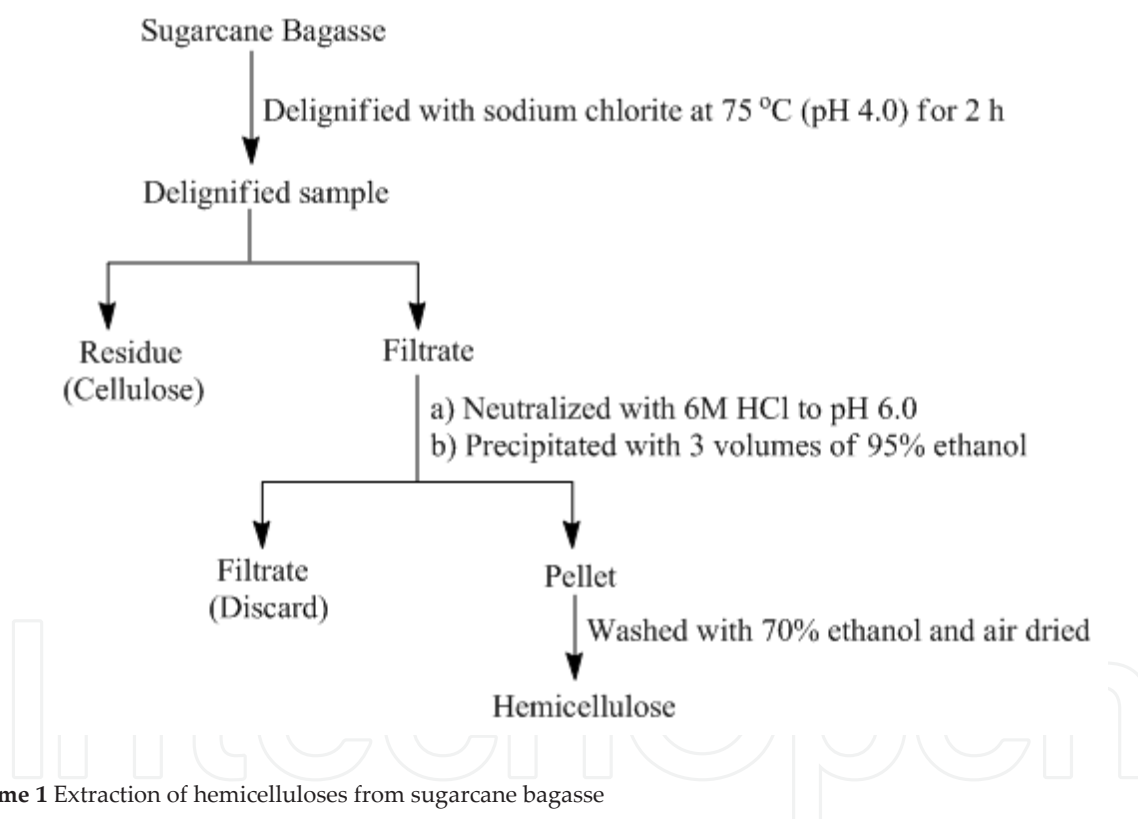
Sugarcane bagasse (SCB) was obtained from a local sugar factory (Guangzhou, China). It was dried in sunlight and then cut into small pieces. The cut SCB was ground to pass a 0.8-mm screen. It was dried in a cabinet oven with air circulation for 20 h at 50°C.

4-Dimethylaminopyridine (DMAP, 99%) and ϵ -caprolactone (ϵ -CL, 99%) were supplied by Aladdin Reagents Co., Ltd. (Shanghai, China). The ionic liquid 1-butyl-3-methylimidazolium

chloride ($[\text{C}_4\text{mim}]\text{Cl}$, 99%) was purchased from Cheng Jie Chemical Co., Ltd. (Shanghai, China), and dried in vacuum for 48 h at 70°C before used. All other chemicals were of analytical reagent grade and directly used without further purification.

2.2. Isolation and characterization of the native hemicellulose from SCB

Sugarcane bagasse was first delignified with sodium chlorite in acidic solution (pH 4.0, adjusted by 10% acetic acid) at 75°C for 2 h. The hemicelluloses were then extracted from the holocellulose with 10% NaOH for 10 h at 20°C with a liquor ratio of 1 to 20, followed by the acidification of the supernatant to pH 6.0 with 6M HCl and then the precipitation in 3 volumes of 95% ethanol. After filtration, the pellets of the hemicelluloses were washed with acidified 70% ethanol and then air dried. The main procedure of isolation hemicelluloses is shown in Scheme 1.



Scheme 1 Extraction of hemicelluloses from sugarcane bagasse

2.3. Synthesis of Hemicellulose-g-PCL copolymers in $[\text{C}_4\text{mim}]\text{Cl}$

Dry hemicelluloses (0.33 g, 0.005 mol of hydroxyl group in hemicelluloses) were added to $[\text{C}_4\text{mim}]\text{Cl}$ (7.5 g) in a 50-mL dried three-neck flask. The mixture was stirred at 85°C for 1 h under the protection of nitrogen to achieve a homogenous solution. Then, the required quantities of ϵ -CL and DMAP were added gradually over a period of 2 min into the solution. The ROGP reaction was carried out under the protection of nitrogen with vigorous stirring for 24 h. After the required time, the solution was cooled to room temperature and the resultant

graft copolymer was precipitated in excessive ethanol and dialyzed with a 3000-molecular weight dialysis bag in ultrapure water for 7 days. The final product was freeze-dried for 48 h. Each sample was duplicated under the same conditions to reduce errors and confirm the results.

2.4. Characterization of hemicelluloses and hemicellulose-g-PCL copolymers

FT-IR spectra of unmodified hemicelluloses and hemicelluloses-g-PCL copolymers were recorded on an FT-IR spectrophotometer (Tensor 27, Germany) from a KBr disc containing 1% (w/w) finely ground samples in the range of 4000 to 400 cm^{-1} . Thirty-two scans were taken for each sample, with a resolution of 2 cm^{-1} in the transmittance mode.

The ^1H -NMR, ^1H - ^1H COSY, ^{13}C -NMR, and ^1H - ^{13}C HSQC spectra of unmodified hemicellulose and hemicellulose-g-PCL copolymers were recorded from 40 mg samples in 0.5 mL DMSO-d_6 on a Bruker Avance III 400 M spectrometer (Germany) with a 5 mm multinuclear probe. For the ^1H -NMR analysis, the detailed collecting and processing parameters were listed as follows: number of scans, 64; receiver gain, 456; acquisition time, 1.3631 s; relaxation delay, 3.0 s; pulse width, 3.0 s; spectrometer frequency, 400.13 MHz; and spectral width, 6009.6 Hz. For the ^1H - ^1H COSY analysis, the detailed collecting and processing parameters were listed as follows: number of scans, 8; receiver gain, 447; acquisition time, 0.4588 s; relaxation delay, 2.0 s; pulse width, 9.0 s; spectrometer frequency, 400.13/400.13 MHz; and spectral width, 4000.0/4000.0 Hz. For the ^{13}C -NMR analysis, the detailed collecting and processing parameters were listed as follows: number of scans, 2112; receiver gain, 2048; acquisition time, 0.3296 s; relaxation delay, 5.0 s; pulse width, 9.8 s; spectrometer frequency, 100.61 MHz; and spectral width, 25062.7 Hz. For the ^1H - ^{13}C HSQC analysis, the detailed collecting and processing parameters were listed as follows: number of scans, 28; receiver gain, 2050; acquisition time, 0.0639 s; relaxation delay, 2.0 s; pulse width, 8.5 s; spectrometer frequency, 400.13/100.61 MHz; and spectral width, 8012.8/20161.3 Hz. The detailed structure factors of hemicellulose-g-PCL copolymers, including the degree of polymerization of PLA (DP_{PLA}), the molar substitution of PLA (MS), the degree of substitution of PLA (DS), and the weight content of PLA side chains (W_{PLA}), were determined by ^1H -NMR.

The thermal stability of the samples was performed using thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) on a Q500 thermogravimetric analyzer (TA, USA). Samples weighing between 9 and 11 mg were heated from room temperature to 600°C at a thermal ramp of 10°C/min under nitrogen flow.

The surface morphology was examined by SEM on a field emission microscopy (LEO 1530 VP, LEO, Germany). The samples were prepared by casting few solids onto a mica sheet followed by gold-plating.

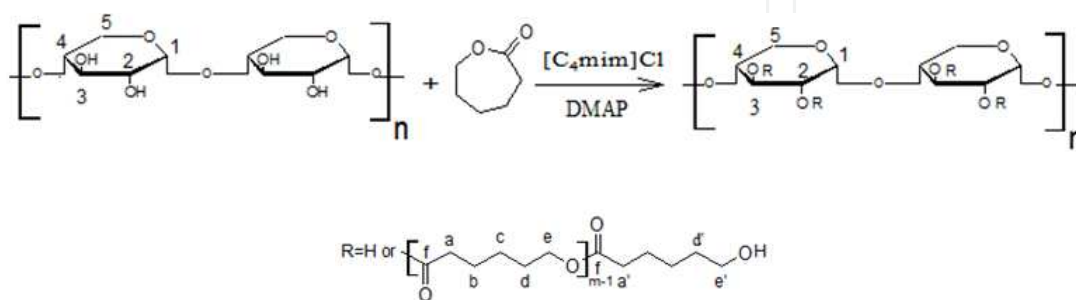
XRD was determined on a D/Max-III X-ray diffractometer (Rigaku, Japan) equipped with the high-intensity monochromatic nickel-filtered $\text{Cu K}_{\alpha 1}$ radiation ($\lambda=0.154$ nm). The operating voltage and current were 40 kV and 40 mA, respectively. Data were collected with diffraction angle 2θ ranging from 5 to 60° with a step size of 0.04° and time per step of 0.2 s at room temperature.

3. Results and discussion

3.1. Synthesis of hemicellulose-g-PCL copolymers in $[C_4mim]Cl$

DMAP and ϵ -CL could be easily dissolved in $[C_4mim]Cl$ within several minutes. Therefore, the homogeneous ROGP reaction of ϵ -CL onto hemicelluloses was performed with DMAP as a catalyst, and a schematic reaction is shown in scheme 2. The effects of reaction conditions, including reaction temperature, the molar ratios of ϵ -CL to anhydroxylose units (AXU) in hemicelluloses, and the dosage of DMAP catalyst on the detailed structure factors, were investigated. Table 1 shows the preparation conditions of hemicellulose-g-PCL copolymers and their detailed structural factors calculated from 1H -NMR.

According to the results in Table 1, an increase in reaction temperature from 110 °C to 120 °C resulted in an increase in DS from 0.03 to 0.09, DP from 1.39 to 1.45, MS from 0.04 to 0.13 and W_{PCL} from 3.33% to 10.09%, which was probably due to the favorable effect of temperature on the molecule motion and collision with the increased temperature. However, further improvement of reaction temperature from 120 °C to 130 °C led to a decrease in DS from 0.09 to 0.06, DP from 1.45 to 1.26, MS from 0.13 to 0.07 and W_{PCL} from 10.09% to 5.71%, probably due to the increased degradation of hemicelluloses in ionic liquid at a higher temperature under the given conditions. The DS, DP, MS and W_{PCL} of the products remarkably increased from 0.09 to 0.22, 1.45 to 1.48, 0.13 to 0.32 and 10.09% to 21.65%, respectively, with an increase in the dosage of DMAP catalyst from 2% to 3%, indicating the good catalytic ability of DMAP for ROGP of ϵ -CL onto hemicelluloses in $[C_4mim]Cl$; while it significantly decreased with a further increase in DMAP dosage to 4%, indicating the detrimental effects of excessive DMAP, which was probably due to the fact that the strong basicity of DMAP inhibited the attachment of PCL onto hemicelluloses. Increasing the molar ratio of ϵ -CL to AXU in hemicelluloses from 1:1 to 3:1 resulted in an improvement of DS from 0.04 to 0.22, DP from 0.93 to 1.48, MS from 0.04 to 0.32 and W_{PCL} from 3.34% to 21.65%, which was probably due to the greater availability of ϵ -CL in the proximity of the reactive hydrogel groups in hemicelluloses at a higher molar ratio of ϵ -CL to AXU. However, a further increase in the molar ratio of ϵ -CL to AXU from 3:1 to 5:1 led to decrease in DS, DP, MS and W_{PCL} , which was probably due to the quick self-polymerization of ϵ -CL.



Scheme 2. The ring opening graft copolymerization of ϵ -CL onto hemicelluloses in $[C_4mim]Cl$ with DMAP as a catalyst

Sample No.	Temp (°C)	Catalyst (wt%)	ϵ -CL/AXU	Time (h)	DP _{PCL} ^a	MS ^b	DS ^c	W ^d _{PCL}
1	110	2%	3:1	24	1.39	0.04	0.03	3.33%
2	120	2%	3:1	24	1.45	0.13	0.09	10.09%
3	130	2%	3:1	24	1.26	0.07	0.06	5.71%
4	120	3%	3:1	24	1.48	0.32	0.22	21.65%
5	120	4%	3:1	24	1.39	0.03	0.02	2.52%
6	120	3%	1:1	24	0.93	0.04	0.04	3.34%
7	120	3%	2:1	24	1.26	0.07	0.06	5.70%
8	120	3%	4:1	24	1.38	0.21	0.13	13.45%
9	120	3%	5:1	24	1.29	0.11	0.08	8.68%

^a The degree of polymerization of PCL, calculated by ¹H-NMR.

^b Molar composition in the graft copolymer, calculated by ¹H-NMR.

^c The degree of substitution of the copolymer, calculated by ¹H-NMR.

^d The PCL content, calculated by ¹H-NMR.

Table 1. Properties of hemicellulose-g-PCL copolymers under various conditions in [C₄mim]Cl.

3.2. FT-IR spectra

The FT-IR spectra of the isolated hemicelluloses and hemicellulose-g-PCL copolymer samples 2 and 4 are shown in Figure 1. The sharp peak at 893 cm⁻¹ is indicative of typical β -anomers, indicating the primary β -glycosidic linkages between the sugar units in the hemicellulosic fractions [26]. The strong absorption band at 1045 cm⁻¹ is largely due to the C-O stretching in the C-O-C linkages [26]. The small band at 1252 cm⁻¹ originates from the C-O antisymmetric stretching in ester. The band at 1382 cm⁻¹ corresponds to the C-H bending, and that at 1638 cm⁻¹ originates from the bending mode of the absorbed water. The peak at 1736 cm⁻¹ is the characteristic absorption of C=O stretching. The characteristic absorbance at 3431 cm⁻¹ is assigned to the hydroxyl group stretching vibrations, and that at 2910 cm⁻¹ is attributed to the C-H stretching vibrations. In the FT-IR spectra of hemicellulose-g-PCL copolymers, the increased intensities of the bands at 2910, 1738, 1252, and 1170 cm⁻¹, from C-H stretching, C=O stretching, C-O antisymmetric stretching, and C-O-C vibration, respectively, were observed compared with those in unmodified hemicelluloses, indicating the successful modification of hemicelluloses in [C₄mim]Cl under the given conditions.

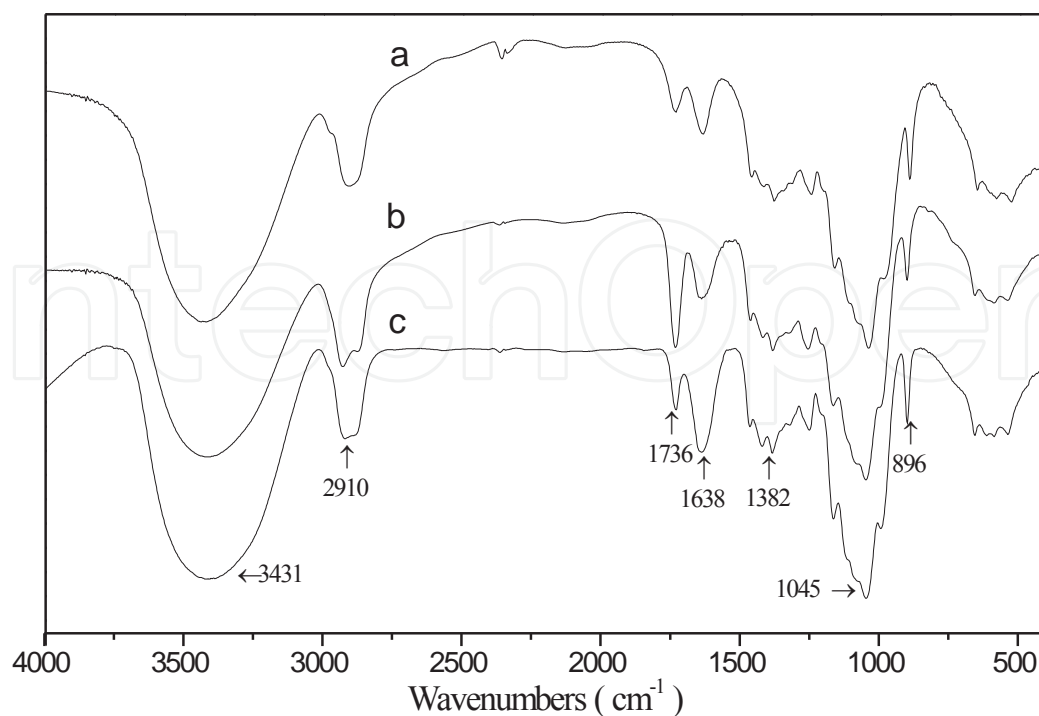


Figure 1. FT-IR spectra of unmodified hemicelluloses (spectrum a) and hemicellulose-g-PCL copolymer samples 2 (spectrum b) and 4 (spectrum c) prepared in $[C_4mim]Cl$

3.3. 1H -NMR, 1H - 1H COSY, ^{13}C -NMR and 1H - ^{13}C HSQC spectra

Figure 2 shows the 1H -NMR spectrum of hemicellulose-g-PCL copolymer sample 2. The resonance peaks derived from the protons of xylan appear at 4.26, 3.03, 3.25, 3.49, 3.17 and 3.78 ppm, assigned to H-1, H-2, H-3, H-4, H-5a and H-5e, respectively[31]. The signals from the methylene proton in PCL appeared at 2.25 ppm ($-COCH_2-$, a), 1.53 ppm ($-CH_2-$, b, d), 1.30 ppm ($-CH_2-$, c), 1.41 ppm ($-CH_2-$, d'), 3.87 ppm ($-CH_2O-$, e), 3.38 ppm ($-CH_2O-$, e') and 4.39 ppm ($-CH_2OH-$, e', end unit) [17]. These observations confirmed the attachment of PCL onto hemicelluloses in ionic liquid $[C_4mim]Cl$. In addition, the signals at 4.53 and 4.87 ppm are associated with the protons at substituted C-2 and C-3 positions, respectively, confirming the attachment of PCL on C-2 and C-3 positions in AXU. Meanwhile, the detailed structural factors of hemicellulose-g-PCL copolymers, including DS, MS, DP_{PLA} , and W_{PLA} , could be calculated from the peak intensity of corresponding signals based on the following equations:

$$DS = \frac{CL_{Terminal}}{AXU} = \frac{I_{e'}/2}{I_{H4}} = \frac{(I_a - I_e)}{I_{H4}} \quad (1)$$

$$MS = \frac{CL}{AXU} = \frac{I_a}{2I_{H4}} \quad (2)$$

$$DP = \frac{CL_{Total}}{CL_{Terminal}} = \frac{I_{(e+e')}}{I_{e'}} = \frac{I_a}{I_a - I_e} \quad (3)$$

$$W_{PCL} = \frac{114MS}{132 + 114MS} \times 100\% \quad (4)$$

where DS is the degree of substitution of PCL, DP is the degree of polymerization of PCL, MS is the molar substitution of PCL, W_{PCL} is the weight content of PCL side chains, AXU is anhydroxylose unit, $CL_{Terminal}$ is the end unit of PCL, CL_{Total} is the total units of PCL, 2 is two protons in each methylene group, I_e , $I_{e'}$ and I_a are the integral area of the resonances of the corresponding methylene protons at e, e', and a positions of PCL, and I_{H4} is the integral area of the resonance assigned to H_4 of AXU. The 114 g mol^{-1} and 132 g mol^{-1} in equation (4) are the molecular weight of ϵ -caprolactone and the molecular weight of xylan unit, respectively.

The DS, MS, $DP_{PLA'}$ and W_{PLA} values calculated from $^1\text{H-NMR}$ are listed in Table 1. The results indicated that the xylan derivatives with DS 0.02–0.22, DP 0.93–1.48, MS 0.03–0.32 and W_{PCL} 2.52–21.65% were obtained under the selected conditions, lower than those of cellulose-g-PCL prepared in [Bmim]Cl [18]. Considering the linear macromolecular structure of cellulose with more hydroxyl groups available, which allowed for more side chains attached on the biopolymer, the estimated DS, MS, $DP_{PLA'}$ and W_{PLA} values of hemicellulose-g-PCL copolymers in the present study were reasonable and acceptable. In addition, the different calculation equation based on the different assignments of the typical proton signals [18] was also responsible for the differences of DS, MS, $DP_{PLA'}$ and W_{PLA} of the copolymers in ionic liquids.

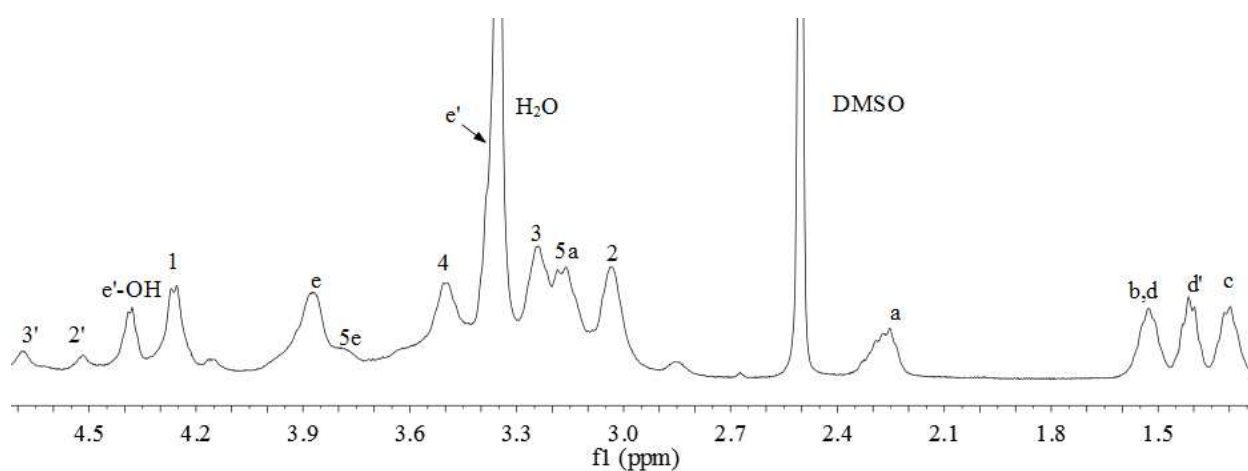


Figure 2. $^1\text{H-NMR}$ spectrum of hemicellulose-g-PCL copolymer sample 2

To confirm the correct assignment of the primary proton signals of the attached PCL side chains, Figure 3 shows the $^1\text{H-}^1\text{H}$ COSY spectrum of hemicellulose-g-PCL copolymer sample 2. To clearly show the cross-correlations of the protons on the attached PCL side chains, the

spectrum is illustrated at higher contour level and as a result the primary signals in AXU and their cross-correlations are not shown. The cross-correlations of PCL side chains, a/b, b/c, c/d', d'/e', e'/e'-OH, were clearly observed, indicating the assignment of the proton signals was correct. Moreover, the cross-correlations for repeating unit indicated the DP of xylan-g-PCL copolymers was over 1, which was corresponded to the results in Table 1.

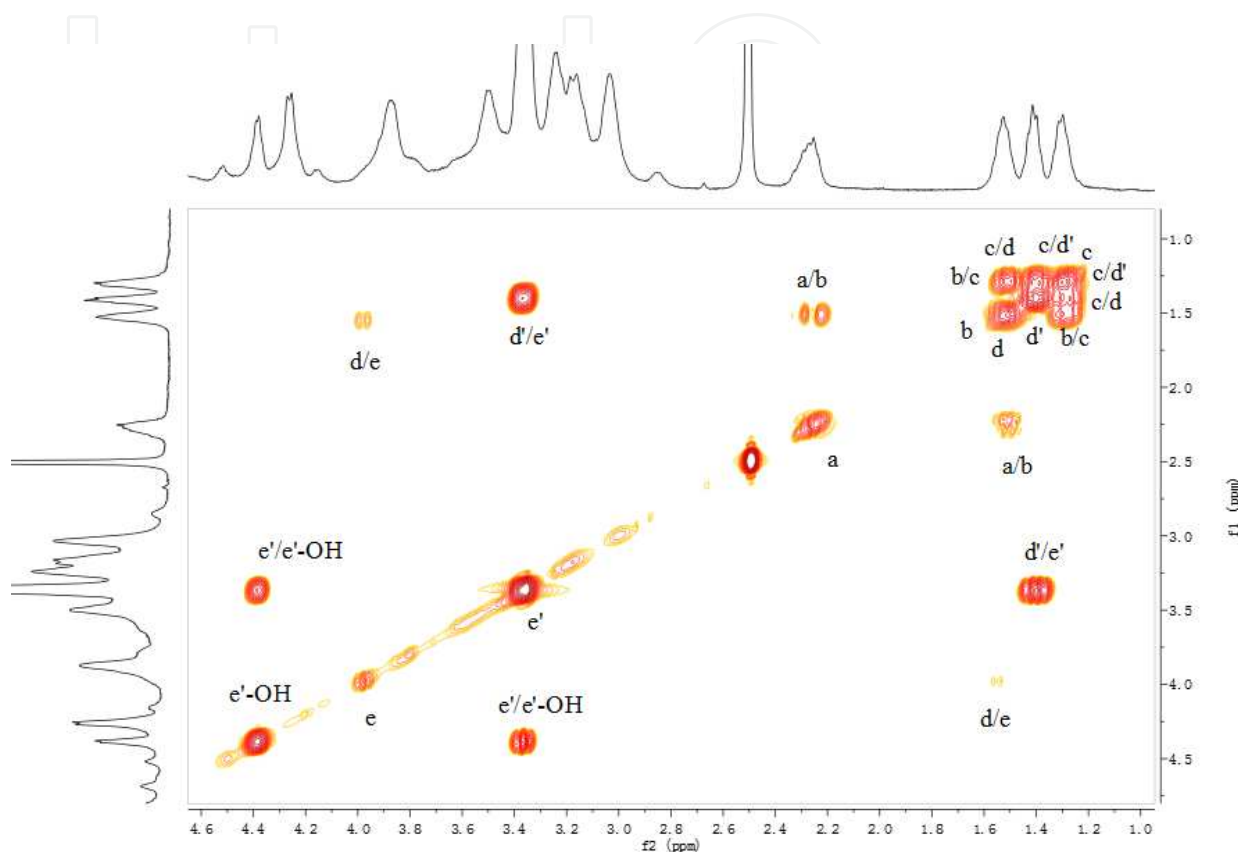


Figure 3. ^1H - ^1H COSY spectrum of hemicellulose-g-PCL copolymer sample 2

Figure 4 illustrates the ^{13}C -NMR spectra of unmodified hemicelluloses (A) and hemicellulose-g-PCL copolymer sample 2 (B). In Figure 4A, the five major signals at 101.8, 75.6, 74.4, 73.4, and 63.5 ppm correspond to C-1, C-4, C-2, C-3, and C-5 of the 1,4-linked β -D-Xylp (xylopyranose) units, respectively [32]. The signals at 97.6, 71.6, 69.9, 82.4, 171.7, and 59.1 ppm can be assigned to C-1, C-3, C-2, C-4, C-6, and the methoxy group of the 4-O-methyl-D-glucuronic acid residue is linked to C-3 of the backbone of the β -D-Xylp units[30]. These results indicated that the native hemicelluloses were composed of 4-O-methyl-D-glucuronic acid-D-xylans. In Figure 4B, the signal at 171.8 ppm is attributed to the carbonyl carbon (in position f) in the PCL segment, and those at 33.5, 24.7, 25.1, 32.1, 32.1, 63.2 and 60.4 ppm correspond to the methylene carbon signals of PCL in the a, b, d, d', e, and e' positions, respectively. The main signals of the β -D-Xylp units are all observed, indicating no significant structural changes in the hemicellulosic backbone. Compared with spectrum A, the relative intensity of the signal of C-3 in the β -D-Xylp units slightly decreased in spectrum B, suggesting that a partial substitution occurred at the C-3 hydroxyl group.

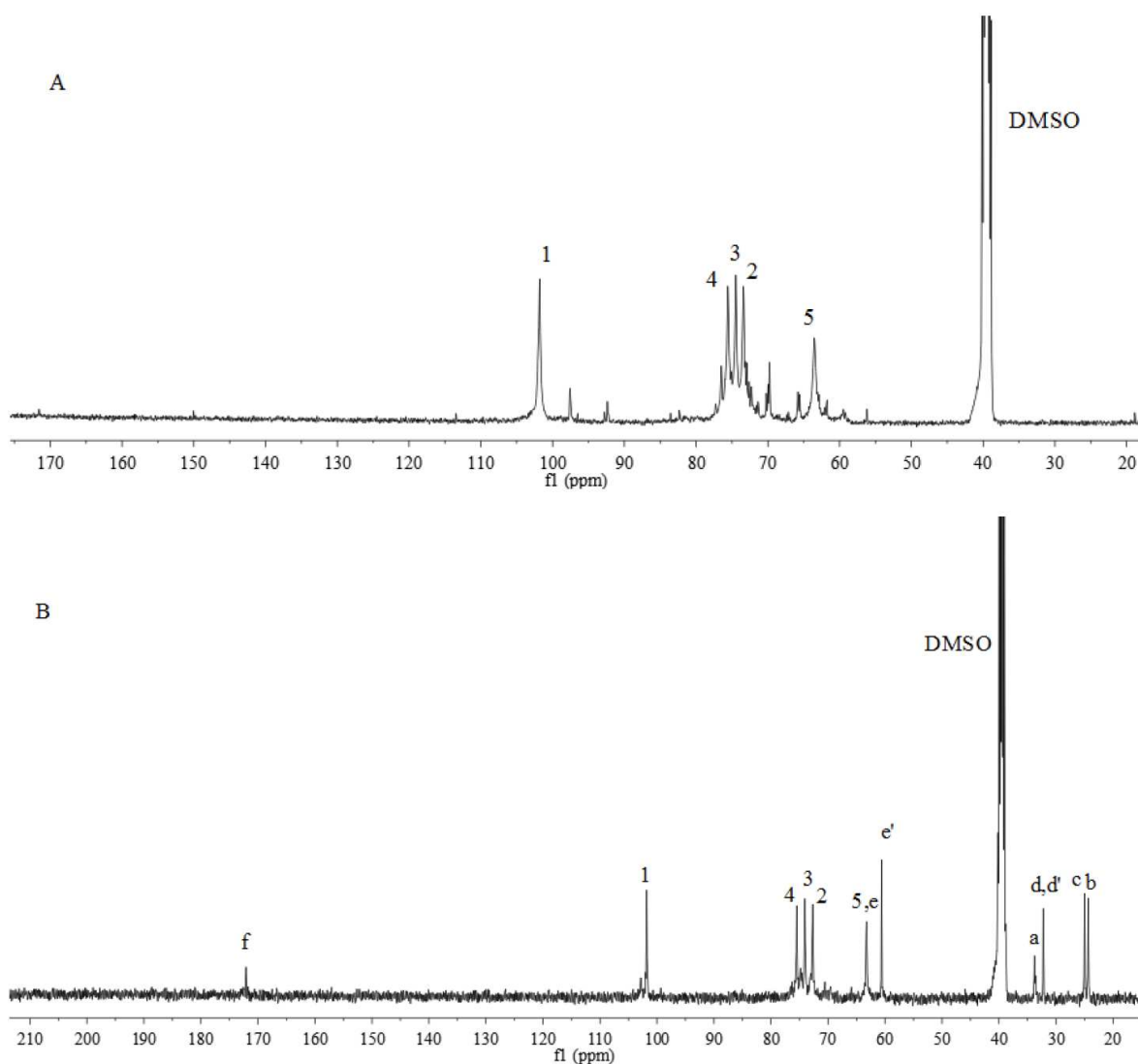


Figure 4. ¹³C-NMR spectra of unmodified hemicelluloses (A) and hemicellulose-g-PCL copolymer sample 2 (B)

¹H-¹³C HSQC provides detailed information of signals overlapped in ¹H- and ¹³C-NMR spectra, and could be applied for qualitative and quantitative analysis of chemical structure. HSQC spectrum of sample 2 was illustrated in Figure 5. To exhibit the primary correlations both unsubstituted and substituted, the spectrum is illustrated at a relatively low contour level. The strong correlations at δ_C/δ_H 33.2/2.26, 24.2/1.52, 24.8/1.30, 31.9/1.38, 32.9/1.52, 60.8/3.39 and 62.7/3.88 ppm are associated with C_a-H_a, C_b-H_b, C_c-H_c, C_d'-H_d', C_d-H_d, C_e'-H_e' and C_e-H_e, respectively, indicated that the PCL side chains were successfully attached onto xylan. Clearly, the strong correlations in carbohydrate region at δ_C/δ_H 102.4/4.24, 72.9/3.02, 73.8/3.23, 75.7/3.49, 63.6/3.79, and 63.6/3.14 ppm are attributed to C₁-H₁, C₂-H₂, C₃-H₃, C₄-H₄, C_{5e}-H_{5e} and C_{5a}-H_{5a} in AXU of xylan, respectively. More importantly, the correlations at δ_C/δ_H 72.7/4.51 and 75.1/4.81 for substituted C₂-H₂ (2') and substituted C₃-H₃ (3'), respectively, provided the possible quantitative estimation of ROGP reaction occurred at C₂ and C₃ positions. Clearly, more PCL side chains were attached to C₃ position than to C₂ position. The integrated resonances for

substituted and unsubstituted C_2/H_2 and C_3/H_3 indicated that 16.34% and 83.66% of PCL side chains were attached to C_2 and C_3 positions of AXU, respectively.

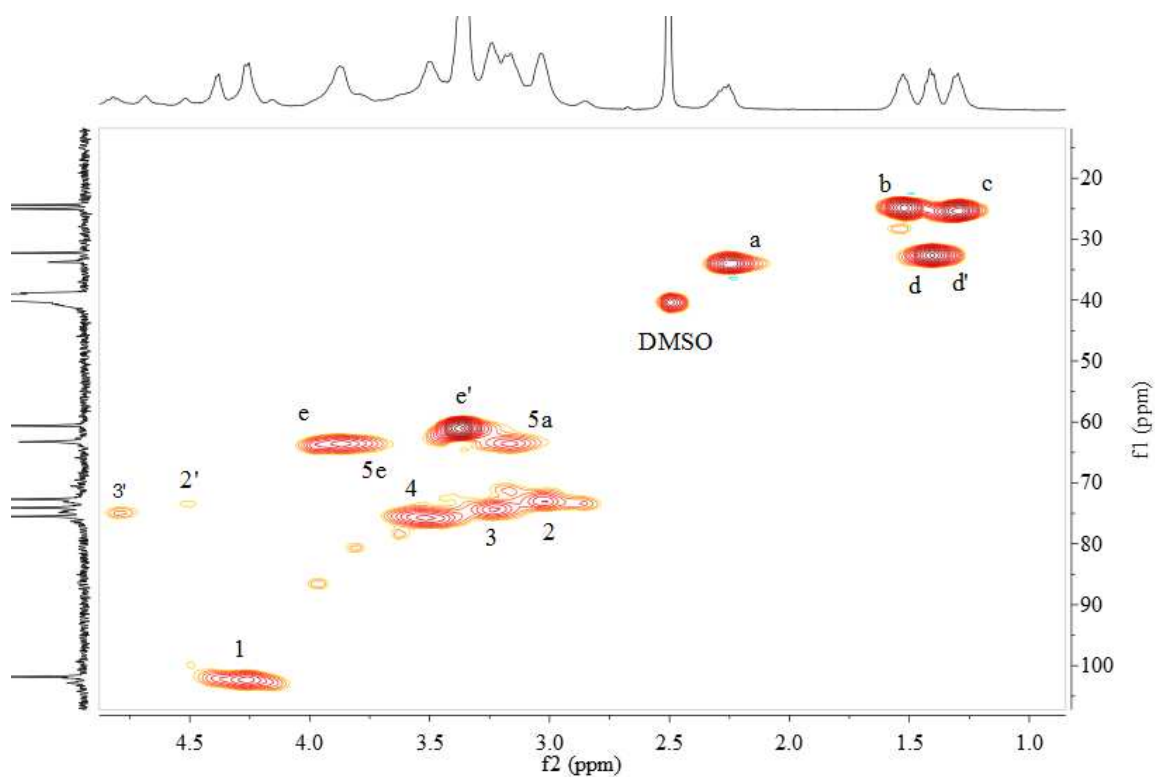


Figure 5. HSQC spectrum of hemicellulose-g-PCL copolymer sample 2

3.4. Thermal analysis

The thermal properties of unmodified hemicelluloses and hemicellulose-g-PCL copolymers were studied using TGA (Figure 6A) in the temperature range from 50°C to 600°C under a nitrogen atmosphere. Clearly, the thermal decomposition can be divided into three distinct stages. In the first stage, the weight loss observed below 100°C was the result of evaporation of moisture. At the second stage, the unmodified hemicelluloses began to decompose at about 215°C, while hemicellulose-g-PCL copolymer samples 2 and 4 started to decompose at about 200°C. The decomposition temperature for a 50% weight loss occurred at 280°C for unmodified hemicelluloses, 275°C for hemicellulose-g-PCL copolymer sample 2, and 270°C for sample 4. In the third stage, the weight marginally decreased after 300°C for unmodified hemicelluloses, after 320°C for sample 2, and after 350°C for sample 4. These results indicated that the thermal stability of hemicellulose-g-PCL copolymers decreased after grafting in ionic liquid compared with that of unmodified hemicelluloses. In addition, complete thermal decomposition of hemicellulose-g-PCL copolymers required either a higher temperature or a longer time.

To further explore the thermal degradation process, derivatives of TGA for the unmodified hemicelluloses and the hemicellulose-g-PCL copolymers were studied, as shown in Figure 6B.

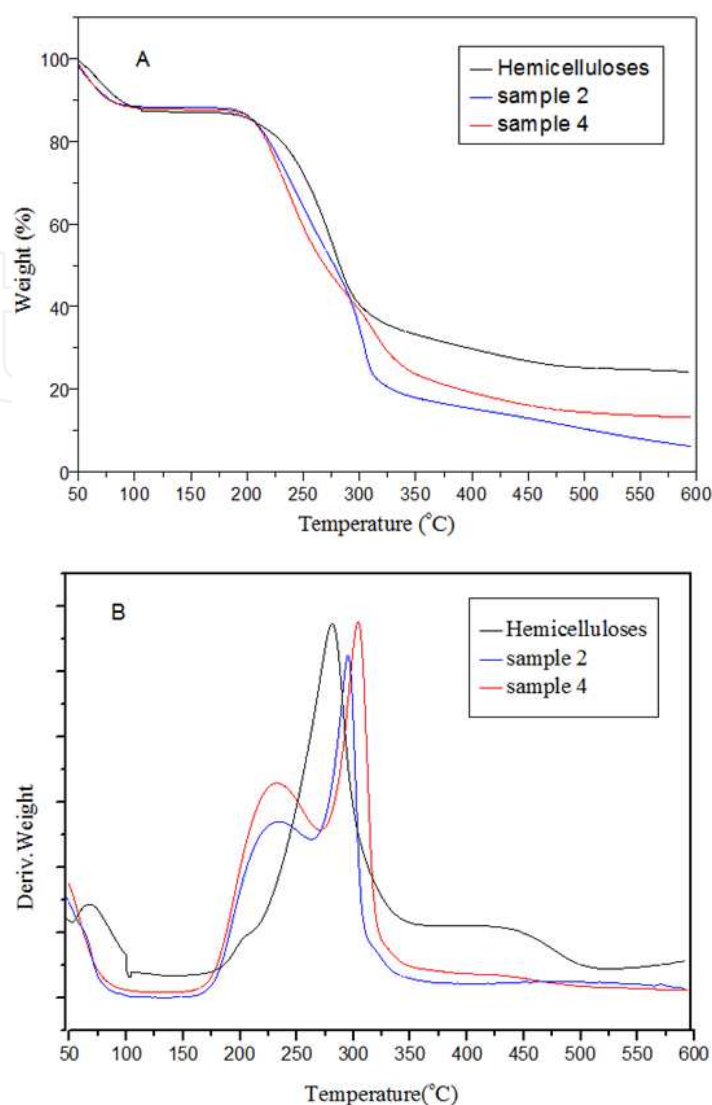


Figure 6. TGA (A) and DTG (B) curves of unmodified hemicelluloses and hemicellulose-g-PCL copolymer samples 2 and 4

DTG_{max} represents the maximum degradation rate and can be used to compare the thermal stability between the samples [33]. Unmodified hemicelluloses showed the maximum degradation rate at about 278°C, while hemicellulose-g-PCL copolymer sample 2 showed two degradation peaks, at 231°C and 293°C. In general, it is impossible to avoid the degradation of biopolymers during dissolution and derivatization in ionic liquids [24,34]. The former DTG_{max} was due to the decomposition of hemicelluloses, providing the evidence of degradation of the hemicellulose substance in ionic liquids. Sample 4 exhibited a similar thermal stability to that of hemicelluloses, with a DTG_{max} at 231 °C, indicating the similar degradation of hemicelluloses in [C₄mim]Cl under the given conditions. These results indicated that the thermal stability of hemicellulose-g-PCL copolymers decreased after grafting in ionic liquid compared with that of unmodified hemicelluloses. The latter DTG_{max} was due to the decomposition of PCL side chains. Compared with sample 2, the second DTG_{max} of sample 4 with

increased attachment of PCL increased to 304°C, indicating improved thermal stability with the enhanced PCL attachment. The higher thermal stability of the attached PCL compared to that of hemicelluloses was confirmed. A similar improved thermal stability of glucuronoxylan from aspen wood was also reported after acetylation [35].

3.5. SEM

To investigate how chemical modification affects the morphology of hemicelluloses, a series of SEM observation of native hemicelluloses and hemicelluloses-g-PCL copolymers are illustrated in Figure 7. The changes of the morphology of the native and modified hemicelluloses were clearly observed with different reaction conditions. The unmodified hemicelluloses showed fluffy block structure, with a smooth and dense surface, and porous structure was clearly observed for the native and modified hemicelluloses. Compared with native hemicelluloses, the all hemicelluloses-g-PCL copolymers displayed more smaller and ruleless lamellar structure when grafting PCL onto it.

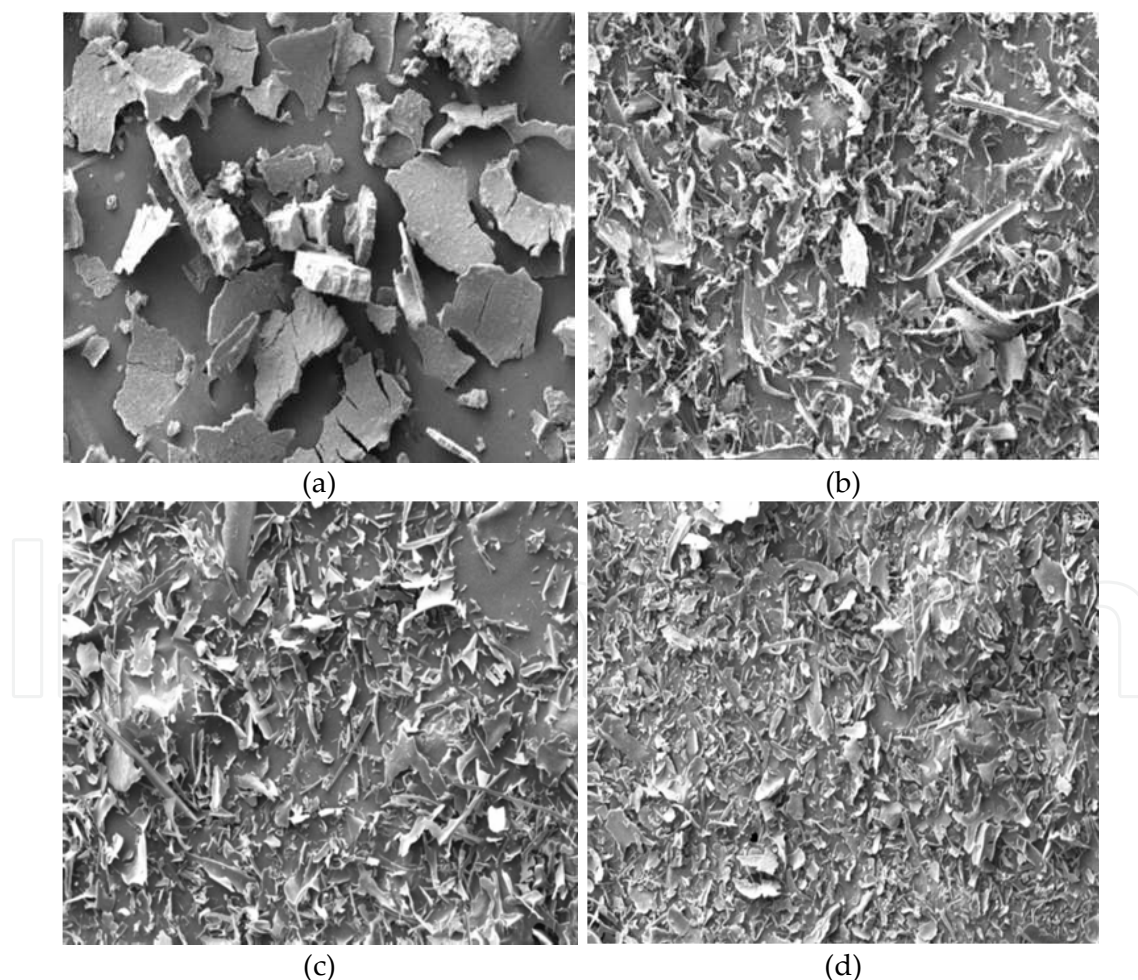


Figure 7. Scanning electron micrographs of the surface of unmodified hemicelluloses (a) and hemicelluloses-g-PCL copolymer samples 2 (b), 4 (c) and 8 (d)

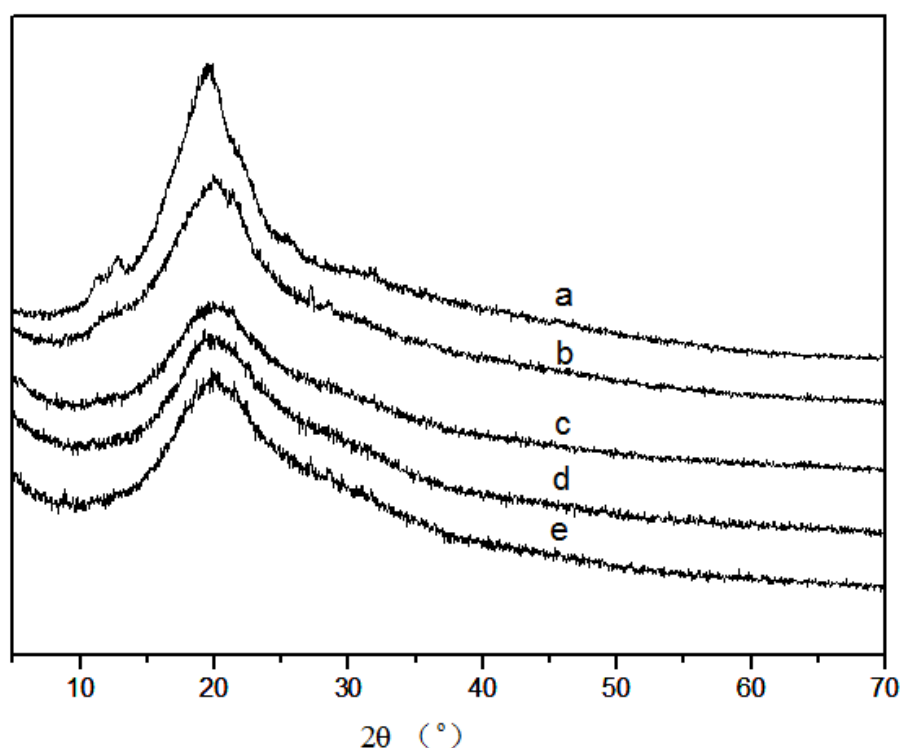


Figure 8. X-ray diffraction patterns of unmodified hemicelluloses (a) and hemicelluloses-g-PCL copolymers (b), 4 (c), 8 (d) and 9 (e)

3.6. XRD

The crystal structure of hemicelluloses and hemicelluloses-g-PCL copolymers were studied using X-ray diffraction analysis and the X-ray diffraction patterns are shown in Figure 8. In spectrum a of native hemicelluloses, there are two small significant diffraction peaks at 2θ 11.2° and 12.4° , and a strong peak at 19.1° . The strong diffraction peak are shifted in the spectra of hemicelluloses-g-PCL samples 2, 4, 8, and 9 to 20.2° (b), 20.9° (c), 20.4° (d) and 19.8° (e), respectively, and the intensity of diffraction patterns decreased. The small peaks at 11.2° and 12.4° could not be observed in the diffraction patterns of hemicelluloses-g-PCL copolymers. These changes suggested that the original crystalline structure of hemicelluloses was disrupted by modification under homogeneous conditions in ionic liquid.

4. Conclusions

Homogeneous ring opening graft polymerization (ROGP) of ϵ -caprolactone (ϵ -CL) onto hemicelluloses was achieved using 4-dimethylaminopyridine (DMAP) as a catalyst in 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$) ionic liquid. The detailed structural factors determined from 1H -NMR indicated that the optimized synthesis of hemicellulose-g-PCL copolymers with a PCL content of 21.65% was performed at $120^\circ C$ for 24 h with the molar ratio of ϵ -CL to AXU 3:1 and 3% DMAP. The results from FT-IR, 1H -NMR, ^{13}C -NMR, COSY and

HSQC analyses confirmed the attachment of PCL to hemicelluloses. TGA/DTG suggested the decreased thermal stability of hemicelluloses after ROGP in $[\text{C}_4\text{mim}]\text{Cl}$ and confirmed the higher thermal stability of the attached PCL than that of hemicelluloses. Considering the good biodegradability of hemicellulose and PCL, this kind of hemicellulose-g-PCL copolymers could be used as environmentally friendly materials.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (31170550), Program for New Century Excellent Talents in University (NCET-11-0154), the Fundamental Research Funds for the Central Universities, and the National Program for Support of Top-notch Young Professionals.

Author details

X.Q. Zhang¹, M.J. Chen¹, H.H. Wang¹, X.X. Wen¹, C.F. Liu^{1*} and R.C. Sun^{1,2}

*Address all correspondence to: chliu@scut.edu.cn

1 State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, P. R. China

2 Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing, P. R. China

References

- [1] Lönnberg H, Zhou Q, Brumer H, Teeri TT, Malmström E, Hult A. Grafting of cellulose fibers with poly(ϵ -caprolactone) and poly(l-lactic acid) via ring-opening polymerization. *Biomacromolecules* 2006;7(7): 2178-2185.
- [2] Roy D, Semsarilar M, Guthrie JT, Perrier S. Cellulose modification by polymer grafting: A review. *Chemical Society Reviews* 2009;38(7): 2046-64.
- [3] Tosh B, Routray CR. Grafting of cellulose based materials: A review. *Chemical Science Review and Letters* 2014;10.
- [4] Söderqvist Lindblad M, Albertsson A-C, Ranucci E, Laus M, Giani E. Biodegradable polymers from renewable sources: Rheological characterization of hemicellulose-based hydrogels. *Biomacromolecules* 2005;6(2): 684-690.

- [5] Yang JY, Zhou XS, Fang J. Synthesis and characterization of temperature sensitive hemicellulose-based hydrogels. *Carbohydrate Polymers* 2011;86(3): 1113-1117.
- [6] Hansen NML, Plackett D. Sustainable films and coatings from hemicelluloses: A review. *Biomacromolecules* 2008;9(6): 1493-1505.
- [7] Puls J, Schröder N, Stein A, Janzon R, Saake B. Xylans from oat spelts and birch kraft pulp. *Macromolecular Symposia* 2005;232(1): 85-92.
- [8] Sarossy Z, Plackett D, Egsgaard H. Carbohydrate analysis of hemicelluloses by gas chromatography-mass spectrometry of acetylated methyl glycosides. *Analytical and Bioanalytical Chemistry* 2012;403(7): 1923-1930.
- [9] Edlund U, Albertsson AC. A microspheric system: Hemicellulose-based hydrogels. *Journal of Bioactive and Compatible Polymers* 2008;23(2): 171-186.
- [10] Saha B. Hemicellulose bioconversion. *Journal of Industrial Microbiology and Biotechnology* 2003;30(5): 279-291.
- [11] Peng XW, Ren JL, Zhong LX, Sun RC. Homogeneous synthesis of hemicellulosic succinates with high degree of substitution in ionic liquid. *Carbohydrate Polymers* 2011;86(4): 1768-1774.
- [12] Chung YL, Olsson JV, Li RJ, Frank CW, Waymouth RM, Billington SL, Sattely ES. A renewable lignin-lactide copolymer and application in biobased composites. *ACS Sustainable Chemistry & Engineering* 2013;1(10): 1231-1238.
- [13] Chen CY, Chen MJ, Zhang XQ, Liu CF, Sun RC. Per-o-acetylation of cellulose in dimethyl sulfoxide with catalyzed transesterification. *Journal of Agricultural and Food Chemistry* 2014;62(15): 3446-3452.
- [14] Barthel S, Heinze T. Acylation and carbanilation of cellulose in ionic liquids. *Green Chemistry* 2006;8(3): 301-306.
- [15] Carlmark A, Larsson E, Malmström E. Grafting of cellulose by ring-opening polymerisation – a review. *European Polymer Journal* 2012;48(10): 1646-1659.
- [16] Endo T, Shibasaki Y, Sanda F. Controlled ring-opening polymerization of cyclic carbonates and lactones by an activated monomer mechanism. *Journal of Polymer Science Part A: Polymer Chemistry* 2002;40(13): 2190-2198.
- [17] Xu Q, Kennedy JF, Liu L. An ionic liquid as reaction media in the ring opening graft polymerization of ϵ -caprolactone onto starch granules. *Carbohydrate Polymers* 2008;72(1): 113-121.
- [18] Guo YZ, Wang XH, Shen ZG, Shu XC, Sun RC. Preparation of cellulose-graft-poly(ϵ -caprolactone) nanomicelles by homogeneous rop in ionic liquid. *Carbohydrate Polymers* 2013;92(1): 77-83.

- [19] Yuan W, Yuan J, Zhang F, Xie X. Syntheses, characterization, and in vitro degradation of ethyl cellulose-graft-poly(ϵ -caprolactone)-block-poly(L-lactide) copolymers by sequential ring-opening polymerization. *Biomacromolecules* 2007;8: 1101-1108.
- [20] Habibi Y, Dufresne A. Highly filled bionanocomposites from functionalized polysaccharide nanocrystals. *Biomacromolecules* 2008;9(7): 1974-1980.
- [21] Kim MS, Hyun H, Seo KS, Cho YH, Won Lee J, Rae Lee C, Khang G, Lee HB. Preparation and characterization of mpeg-pcl diblock copolymers with thermo-responsive sol-gel-sol phase transition. *Journal of Polymer Science Part A: Polymer Chemistry* 2006;44(18): 5413-5423.
- [22] Youssef Habibi ALG, Nancy Schiltz, Emmanuel Duquesne, Philippe Dubois. Bionanocomposites based on poly(3-caprolactone)-grafted cellulose nanocrystals by ring-opening polymerization. *Journal of Materials Chemistry* 2008;18: 9.
- [23] Krouit M, Bras J, Belgacem MN. Cellulose surface grafting with polycaprolactone by heterogeneous click-chemistry. *European Polymer Journal* 2008;44(12): 4074-4081.
- [24] El Seoud OA, Koschella A, Fidale LC, Dorn S, Heinze T. Applications of ionic liquids in carbohydrate chemistry: A window of opportunities. *Biomacromolecules* 2007;8(9): 2629-2647.
- [25] Swatloski RP, Spear SK, Holbrey JD, Rogers RD. Dissolution of cellulose with ionic liquids. *Journal of the American Chemical Society* 2002;124(18): 4974-4975.
- [26] Ayoub A, Venditti RA, Pawlak JJ, Sadeghifar H, Salam A. Development of an acetylation reaction of switchgrass hemicellulose in ionic liquid without catalyst. *Industrial Crops and Products* 2013;44(0): 306-314.
- [27] Li WY, Wu L, Chen D, Liu CF, Sun RC. Dmap-catalyzed phthalylation of cellulose with phthalic anhydride in bmimcl. *BioResources* 2011;6(3): 2375-2385.
- [28] Liu CF, Zhang AP, Li WY, Yue FX, Sun RC. Homogeneous modification of cellulose in ionic liquid with succinic anhydride using n-bromosuccinimide as a catalyst. *Journal of Agricultural and Food Chemistry* 2009;57(5): 1814-1820.
- [29] Biswas A, Shogren RL, Stevenson DG, Willett JL, Bhowmik PK. Ionic liquids as solvents for biopolymers: Acylation of starch and zein protein. *Carbohydrate Polymers* 2006;66(4): 546-550.
- [30] Wang HT, Yuan TQ, Meng LJ, She D, Geng ZC, Sun RC. Structural and thermal characterization of lauroylated hemicelluloses synthesized in an ionic liquid. *Polymer Degradation and Stability* 2012;97(11): 2323-2330.
- [31] Cao XF, Sun SN, Peng XW, Zhong LX, Sun RC. Synthesis and characterization of cyanoethyl hemicelluloses and their hydrated products. *Cellulose* 2013;20(1): 291-301.

- [32] Xu F, Sun JX, Liu CF, Sun RC. Comparative study of alkali-and acidic organic solvent-soluble hemicellulosic polysaccharides from sugarcane bagasse. *Carbohydrate Research* 2006;341(2): 253-261.
- [33] Nadji H, Diouf PN, Benaboura A, Bedard Y, Riedl B, Stevanovic T. Comparative study of lignins isolated from alfa grass (*stipa tenacissima* l.). *Bioresource Technology* 2009;100(14): 3585-3592.
- [34] Ren JL, Sun RC, Liu CF, Lin L, He BH. Synthesis and characterization of novel cationic scb hemicelluloses with a low degree of substitution. *Carbohydrate Polymers* 2007;67(3): 347-357.
- [35] Grondahl M, Teleman A, Gatenholm P. Effect of acetylation on the material properties of glucuronoxylan from aspen wood. *Carbohydrate Polymers* 2003;52(4): 359-366.