

Homogeneous Esterification of Poplar Wood in an Ionic Liquid under Mild Conditions: Characterization and Properties

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Wood meal was completely dissolved under constant conditions (130 °C, 6 h) in the ionic liquid 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl), and the various factors and potential mechanism of the homogeneous esterification of wood in this reaction medium were mainly studied. The physicochemical properties of the esterified wood were also investigated. It has been shown that highly substituted wood esters could be obtained by reacting wood dissolved in [C₄mim]Cl with octanoyl chloride in the presence of triethylamine as a neutralizer. The weight percent gain was arranged from 121.5% to 297.4%. All reactions were performed under mild conditions, low excess of reagent, and a short reaction time compared to the heterogeneous chemical modification. Meanwhile, characterization of the derivatives confirmed that the homogeneous esterification was successfully processed. It was also found that thermal stability and morphological properties of the esterified wood were significantly different from those in previous reports. Octanoylation of wood meal in the [C₄mim]Cl homogeneous system reduced the initial temperature of their thermal degradation and decreased the thermal stability compared to those in unmodified wood meal. Furthermore, the fibrillar appearance of wood meal changed into a relatively more homogeneous macrostructure of the esterified wood. All these results suggested that homogeneous esterification of poplar wood in [C₄mim]Cl would enhance the compatibility and improve the processability of wood with synthetic polymers.

KEYWORDS: CP/MAS ¹³C NMR; esterification; ionic liquid; octanoyl chloride; poplar wood; SEM

INTRODUCTION

Biomass is the most abundant lignocellulosic resource on the planet, and it also presents an abundant carbon-neutral renewable resource for the production of bioenergy and biomaterials. As we know, the main components of lignocellulosic are lignin, cellulose, and hemicelluloses. Lignin, as a network polymer, binds with the carbohydrates (hemicelluloses and cellulose) to form a tight compact structure (1). Therefore, the complex structure of biomass makes it nearly impossible to dissolve in common molecular solvents. Fortunately, recent discoveries have proved that there are some suitable systems that may allow the dissolution of lignocellulosic materials, such as dimethylsulfoxide/tetrabutylammonium (DMSO/TBAF) (2), dimethylsulfoxide/*N*-methylimidazole (DMSO/NMI) (2, 3), dimethylsulfoxide/lithium chloride (DMSO/LiCl) (4), and various ionic liquids (5). However, we must note that the three organic solvent systems based on DMSO are limited to the analysis of the chemical structure of the wood components, especially for lignin. Even worse, these solvents are volatile organic compounds (VOCs). Ionic liquids, on the contrary, have recently received much attention as green (environmentally friendly), designable solvents, which are favorable in light of the growing realization of the need to protect the environment (6).

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The typical characteristics of ionic liquids are their extremely low vapor pressure, inflammableness, and their thermal and chemical stability. As a consequence of these advantages, ionic liquids have been regarded as the solvents of the future (7).

The bridge between ionic liquids and biomass had been built by Rogers' research group in 2002 (8). Swatoski et al. found that the ionic liquid 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl) could dissolve cellulose with no prior derivatization in concentrations of up to 300 g L⁻¹ (8, 9). Once reported, the research of biomass, especially of carbohydrate chemistry, has boomed in recent years. More information about the applications of ionic liquids in carbohydrate chemistry could be acquired from recent reviews (10–12). However, can ionic liquids dissolve wood? This critical question was also asked by Rogers' research group in 2006. Fort et al. (13) have reported a simple and novel alternative approach for the processing of lignocellulosic materials that relies on their solubility in solvent systems based on the ionic liquid [C₄mim]Cl. After that, a new question emerges accordingly. Can other ionic liquids dissolve wood? To answer this question, many researchers and groups carried out a number of experiments in their endeavors. For instance, Zavrel et al. (14) have presented two high-throughput systems for the fast screening of the dissolution power of different ionic liquids. It was observed that AmimCl is the most effective ionic liquid for dissolving wood chips. Sun et al. (15) have reported that both softwood (southern

yellow pine) and hardwood (red oak) can be completely dissolved in the ionic liquid 1-ethyl-3-methylimidazolium acetate ([C₂mim]-OAc) after mild grinding. Among the various studies, the research group of Argyropoulos initially investigated the details of the dissolution of lignocellulosic in ionic liquids, and they have defined the various variables that determine its solubilization efficiency in ionic liquids (16, 17).

Clearly, we could note that almost all previous reports about the dissolution of lignocellulosic in ionic liquids were mainly adopted as pretreatment technologies. For example, [C₂mim]-OAc and [C₂mim][ABS] had been used as pretreatment solvents to extract lignin from wood flour and bagasse (18, 19). Another significant application might be the hydrolysis of lignocellulosic in the systems based on ionic liquids (20–22). However, much less has been described about in situ derivatization of lignocellulosic in the ionic liquids homogeneous systems when compared to carbohydrate. Meanwhile, over the past few years, the production of fiber/thermoplastic composites with lignocellulosic fibers has been found to be important, economical, and environmental. Thermofluidity has been observed when wood samples were esterified with appropriate acid chlorides in N₂O₄-dimethylformamide-pyridine medium, and increasing the chain length of the alkyl substituent led to a decrease in the apparent melting temperature. In general, the esterification agents must contain at least six atoms of carbon to improve the thermoplastic properties of wood (23, 24). Actually, Argyropoulos et al. (25, 26) have investigated the thorough chemical modification of wood-based lignocellulosic materials in ionic liquids, and highly compatible wood thermoplastic composites were obtained. But when considering the limited utilization of wood arising from its low thermoplasticity and low efficiency as well as the use and/or release of environmentally unsustainable reagents during the heterogeneous chemical modification of wood, we could clearly draw a conclusion that more attention should be paid to the homogeneous, efficient, and environmentally friendly chemical modification of wood.

In this context, we completely dissolved the wood meal under constant conditions in the ionic liquid [C₄mim]Cl and mainly studied the various factors and possible mechanism of the homogeneous esterification of wood in this reaction medium. The physicochemical properties of the esterified wood were also investigated.

MATERIALS AND METHODS

Materials. A fast-growing poplar tree, 7 years old, was harvested from the experimental farm of Beijing Forest University. The outer and inner bark were peeled off, and the wood was cut into small pieces and then dried at 60 °C in an oven for 16 h. The wood sample was then ground to pass through a 0.8 mm size screen. The powder was dewaxed with toluene-ethanol (2:1, v/v) in a Soxhlet instrument for 6 h. The dewaxed sample was further dried at 60 °C in an oven for 16 h and stored at 5 °C before ball milling. Rotary ball milling was performed in a 2-L porcelain jar in the presence of 68 porcelain balls (15 mm in diameter) according to a previous report (27). The mild milling process was conducted at room temperature for up to 48 h with a rotation speed of 70 rpm. The ionic liquid [C₄mim]Cl (≥99%) used was purchased from Chemer, Hangzhou, China. Octanoyl chloride, triethylamine, and methanol were of reagent grade and used as obtained without purification.

Dissolution of Wood in [C₄mim]Cl. To ensure the complete dissolution of the mild ball-milled wood meal in the ionic liquid [C₄mim]Cl, the constant conditions of the dissolution process were set according to a previous report (16). Wood meal (0.50 g) was added to 10 g of [C₄mim]Cl in a 50 mL dried three-neck flask. The mixture was then placed into an oil bath and heated on a hot plate (IKA RCT basic, Germany) with vigorous magnetic stirring (600 rpm) at 130 °C for 6 h under a N₂ atmosphere.

Esterification of Wood in [C₄mim]Cl. After the complete dissolution of wood meal in [C₄mim]Cl, the dissolved wood was cooled to about 80 °C. Triethylamine was added to the cooled dissolved wood under

Table 1. Esterification Conditions Examined for the Derivatization of Poplar Wood in the Ionic Liquid 1-Butyl-3-methylimidazolium Chloride

number	molar ratio ^a	reaction temperature (°C)	reaction time (h)	WPG (%)	hydroxyl group substituted (mmol g ⁻¹)
E1	1.0	90	2.0	121.5	9.6
E2	1.5	90	2.0	187.0	14.8
E3	2.0	90	2.0	258.0	20.5
E4	2.5	90	2.0	297.4	23.6
E5	2.0	80	2.0	267.1	21.2
E6	2.0	100	2.0	264.8	21.0
E7	2.0	90	0.5	226.6	18.0
E8	2.0	90	1.0	230.5	18.3
E9	2.0	90	3.0	267.4	21.2

^a Molar ratio of octanoyl chloride and triethylamine to hydroxyl groups in poplar wood (based on 14.6 mmol g⁻¹ of hydroxyl groups present in poplar wood).

vigorous magnetic stirring (600 rpm) for 5 min, followed by equimolar octanoyl chloride (Table 1). In the present article, triethylamine was used as a neutralizer to counteract the HCl generated during the esterification process. This solution was then placed into an oil bath at different reaction temperature and time according to the conditions listed in Table 1. Isolation of the derivative was carried out by precipitation of the heated solution into methanol (100 mL), followed by water (100 mL) under vigorous magnetic stirring (600 rpm) at 50 °C for 2 h. The solid product was filtered on a glass filter (G3) and then thoroughly rinsed with methanol/water (1/1, v/v mixture). The weight gain (WG) was calculated from the oven-dry weights (60 °C for 16 h) before and after esterification.

Weight percentage gain (WPG) was calculated according to eq 1:

$$\text{WPG (\%)} = [(W_m - W_u)/W_u] \times 100 \quad (1)$$

where W_m is the oven-dry weight of the modified wood meal and W_u is the corresponding oven-dry weight of the unmodified wood meal.

The degree of hydroxyl substitution (in mmol g⁻¹ oven-dry wood meal) was calculated according to eq 2:

$$\text{OH groups substituted} = \{[(W_m - W_u)/W_u]/(M_w - 1)\} \times 1000 \quad (2)$$

where M_w is the molecular weight of the octanoyl group (127 g mol⁻¹), and a value of 1 is subtracted from this to take into account of the loss of the OH proton upon substitution.

Characterization of Wood and Esterified Wood. The FT-IR spectra of the samples were recorded from a KBr disk containing 1% finely ground samples on a Tensor 27 FT-IR spectrophotometer in the range of 4000–400 cm⁻¹. The FT-IR spectra of fresh and recycled ionic liquid were recorded on a Tensor 27 FT-IR spectrophotometer with an Attenuated Total Reflectance (ATR) cell in the range of 4000–400 cm⁻¹. Solid-state cross-polarization/magic angle spinning (CP/MAS) ¹³C NMR spectra of samples were obtained at 100 MHz using a Bruker AV-III 400 M spectrometer (Germany). The sample was packed in 4 mm zirconia (ZrO₂) rotors, and the measurement was performed using a CP pulse program with 1 ms match time and a 2 s delay between transients. The spinning rate was 5 kHz. The ¹H NMR spectra (in CDCl₃) of fresh and recycled ionic liquid were also recorded at 25 °C on a Bruker AVIII 400 MHz spectrometer. X-ray diffractograms were obtained with powdered samples, using an XRD-6000 instrument (Shimadzu, Japan). The diffraction patterns were measured from 2θ = 2 to 35° using Cu-K_α radiation (λ = 1.54 Å) at 40 kV and 30 mA. Thermal stability of the samples was performed using thermogravimetric analysis (TGA) (DTG-60, Shimadzu, Japan). Samples of approximately 10 mg weight were heated in an aluminum crucible to 600 °C at a heating rate of 10 °C min⁻¹ while the apparatus was continually flushed with a nitrogen flow of 30 mL min⁻¹. Changes in morphology before and after esterification were observed by scanning electron microscopy (SEM). For magnification, an S-3400N (HITACHI, Japan) scanning electron microscope was operated at 10 kV acceleration voltages. Prior to imaging, samples were coated with gold-palladium in a sputter coater (E-1010, HITACHI, Japan).

RESULTS AND DISCUSSION

For a long time, the heterogeneous chemical modification of wood has been intensively studied with the aim of improving or

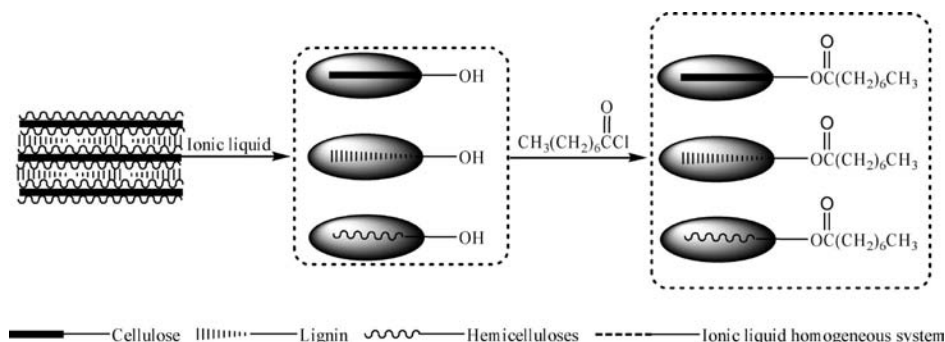


Figure 1. Schematic representation of wood components and the homogeneous esterification reaction carried out in ionic liquid.

modifying its compatibility with thermoplastics, dimensional stability, mechanical properties, moisture content, and resistance to decay. However, these efforts were always achieved at low efficiency, and thus, the potential commercial applications of wood were limited (25). The emergence of homogeneous chemical modification of wood in various ionic liquids has opened up an avenue for exploring the new end-uses. In the present study, in order to investigate the various factors and possible mechanism of the homogeneous chemical modification of wood in ionic liquids, the esterification of wood in the ionic liquid $[C_4mim]Cl$ was processed as described in **Figure 1**, and the results are given in **Table 1**.

Effect of Molar Ratio. In the present article, the theoretical number of OH groups in poplar wood was estimated to be 14.6 mmol g^{-1} according to the method described by Hill and Jones (28). Although there is undoubtedly an error in this estimate, the essential point is that account is taken of the number of moles of reagent reacted with the wood. As can be seen from **Figure 1**, the structure of wood is very complex, such as the crystalline regions of the cellulose and the three-dimensional network of lignin, which makes the amount of OH groups accessible for the chemical modification very limited. However, as Remsing et al. (29) have recently reported, the solvation of carbohydrates in $[C_4mim]Cl$ involves the formation of hydrogen bonds between the nonhydrated chloride ions of the ionic liquid and the sugar hydroxyl protons in a 1:1 stoichiometry. Here, we could presume that in the case of the dissolution of wood in $[C_4mim]Cl$ a similar mechanism is at work. Thereby, the inaccessible OH groups of the cell wall components in the process of heterogeneous chemical modification would be released and exposed to the system when dissolving in the ionic liquid $[C_4mim]Cl$. This means that there will be more OH groups involved in the homogeneous chemical modification.

The data in **Table 1** (E1, E2, E3, and E4) indicate that the molar ratio of octanoyl chloride and triethylamine to the OH groups in the homogeneous esterification process is a very important variable. When this molar ratio increased from 1.0 to 2.5, the value of WPG increased from 121.5% to 297.4% accordingly. It should be noted that these WPG values were much higher as compared to the corresponding values in the previous reports (30, 31). Thiebaut and Borredon (30) and Wu et al. (31) have chemically modified both sugi and oakwood sawdust (2 g) with octanoyl chloride (0.3 mol) in a heterogeneous system at 130°C for 4 h under a continuous nitrogen stream. Coincidentally, in both previous reports, the highest WPG value was about 87%. It was clearly noted that the consumption of the reagent in the present article was just only a quarter when compared to the two aforementioned reports. More importantly, the highest WPG value calculated here was more than three times in comparison to that in the previous heterogeneous system. These comparable data suggested that the esterification of wood in a $[C_4mim]Cl$ homogeneous

system is very efficient. The obvious differences could be due to the increase of accessible OH groups of the cell wall components in the ionic liquid homogeneous system. Besides, the mild ball-milling of the wood sample could also be a reliable reason for this worthy phenomenon because it has been reported that ball-milling leads to partial cleavage of aryl ether linkages and the formation of free phenolic hydroxyl groups (32). According to eq 2, the degree of hydroxyl substitution was arranged from 9.6 to 23.6 mmol g^{-1} . These data further confirmed that the accessible OH groups in the homogeneous system are much higher than those in the heterogeneous system. In addition, as can be seen from **Table 1**, the highest increasing rate of the WPG value was obtained at a molar ratio of 2.0.

Effect of the Reaction Temperature. An examination of the effect of the reaction temperature was also carried out (E3, E5, and E6) for 2.0 h, and the molar ratio used was 2.0. The data in **Table 1** suggest that the reaction temperature between 80 and 100°C results in a similar WPG value (258.0%–267.1%) and the degree of hydroxyl substitution ($20.5\text{--}21.2 \text{ mmol g}^{-1}$) of the derivatives. This means that the reaction temperature just has a slight effect on the homogeneous chemical modification in the present report. As discussed herein, the temperature should be set over the melting point of the ionic liquid used and below the boiling point of the reagent. In addition, the reaction temperature should be high enough to reduce the viscosity of the system. Here, we chose 90°C as the reaction temperature for the discussion of other variables, although the corresponding WPG value was the lowest among the three reaction temperatures. As we know, the reaction temperature is a very critical variable in heterogeneous chemical modification. Thiebaut and Borredon (30) have reported that with an increasing reaction temperature from 100 to 130°C , the WPG value greatly increased from 20% to 87%. It was effortless to understand this difference. As in the heterogeneous system, more energy is needed to promote the penetration of the reagent and accelerate the reaction process.

Effect of the Reaction Time. The effect of the reaction time was investigated by setting different reaction times (E3, E7, E8, and E9) at 90°C , and the molar ratio used was 2.0. As can be seen from **Table 1**, prolonging the reaction time from 0.5 to 3.0 h, the WPG value just increased from 226.6% to 267.4%. The degree of hydroxyl substitution increased from 18.0 to 21.2 mmol g^{-1} . Both increasing tendencies were limited. On the basis of WPG value and the degree of hydroxyl substitution data (**Table 1**), we could draw a conclusion that the variable of the reaction time is not as obvious as the molar ratio. However, the reaction time of octanoylation of wood sawdust in traditional heterogeneous systems is an important variable (30, 31). For instance, Wu et al. (31) have reported that when prolonging the reaction time from 1 to 4 h, the WPG value would increase from 37.5% to 86.5%. The obvious difference might be explained by the different chemical modification mechanisms of the two distinct systems. In the ionic liquid

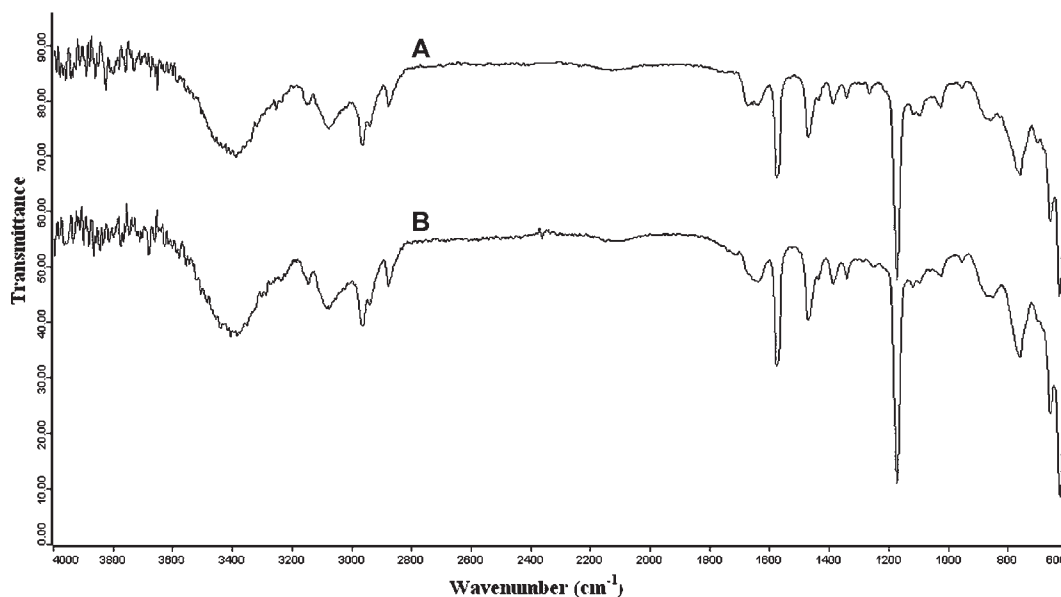


Figure 2. FT-IR spectra of fresh ionic liquid (A) and recycled ionic liquid (B).

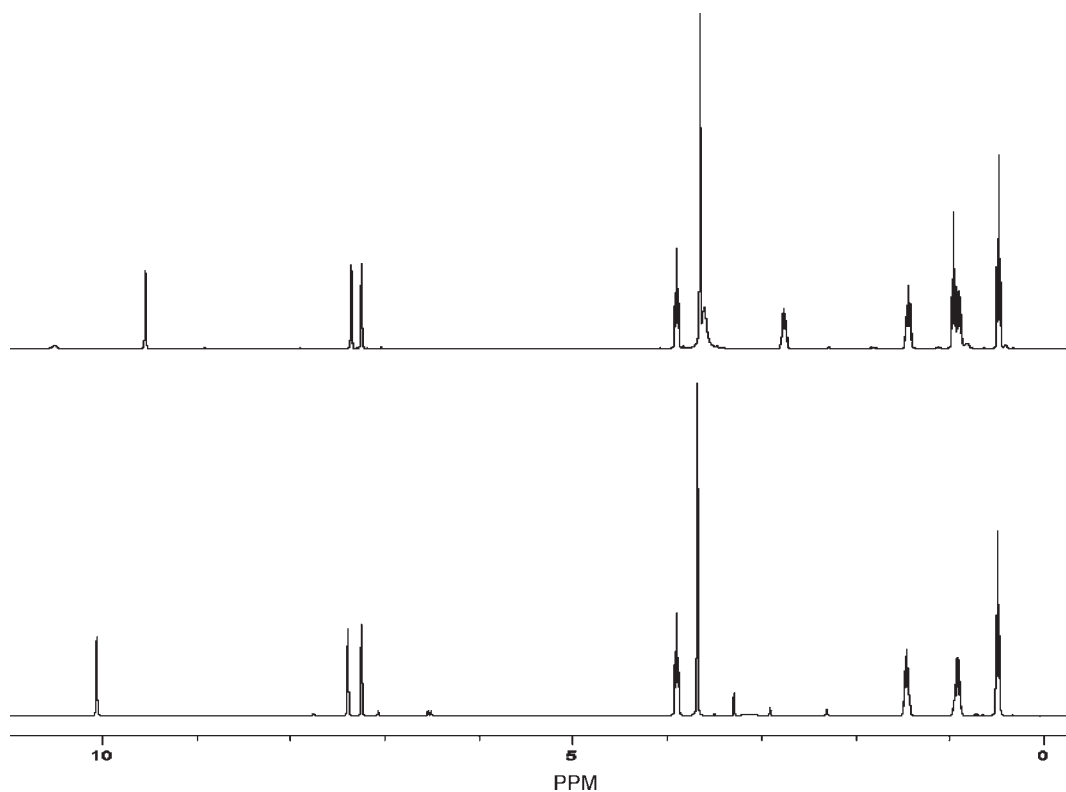


Figure 3. ^1H NMR spectra of fresh ionic liquid (bottom) and recycled ionic liquid (top).

homogeneous system, the OH groups exposed to the system make esterification easy to process. In the heterogeneous system, however, more time would be needed for the reagent to penetrate into the cell wall for reaction with the accessible OH groups during the chemical modification process.

Effect of Ionic Liquid. The recovery and reuse of ionic liquids is now the main challenge in the industrialization of these processes. In the present article, we just recycle the ionic liquid simply by evaporation of the solvents. The FT-IR and ^1H NMR spectra of the fresh and recycled ionic liquid were comparatively characterized (see Figures 2 and 3). No apparent difference could be observed from these two spectra except for the proton signals

from the neutralized triethylamine in the ^1H NMR spectrum of the recycled ionic liquid. These spectra further confirmed that almost all the esterified wood components have been regenerated from the system. Actually, Xie et al. (25) have reported that the wood solubilization and esterification efficiencies of the recycled $[\text{C}_4\text{mim}]\text{Cl}$ from the homogeneous system were rather satisfactory.

FT-IR Analysis. As discussed above, the molar ratio of esterification in the ionic liquid homogeneous system is the most critical variable. Therefore, the derivatives E1, E2, E3, and E4 were chosen to investigate the physicochemical properties of the esterified wood below. The FT-IR spectra of the wood meal and

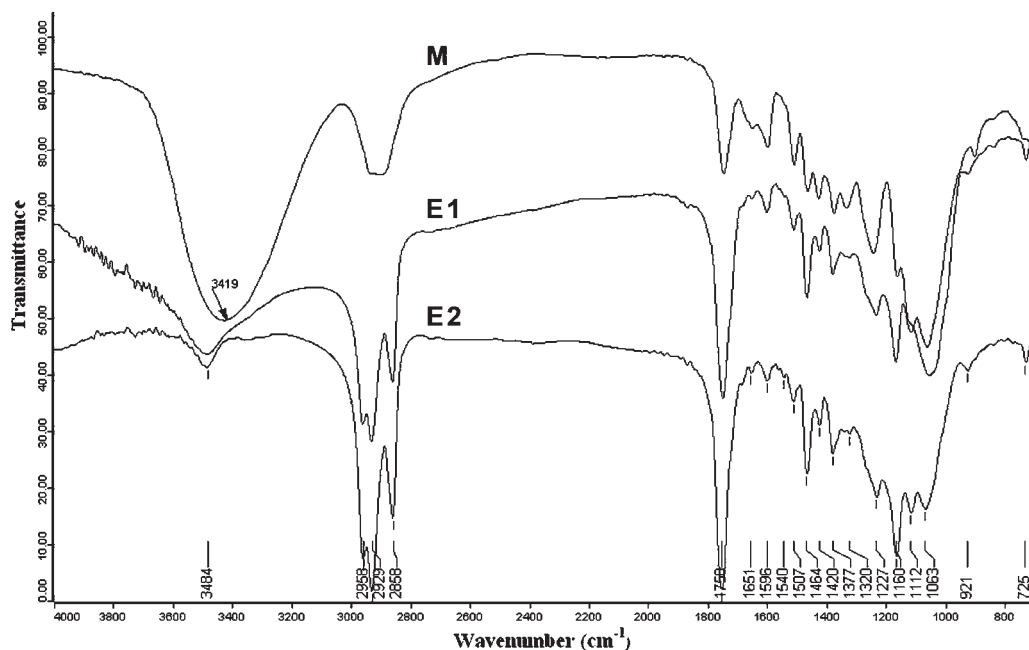


Figure 4. FT-IR spectra of wood meal (M); esterified wood with 121.5% WPG (E1); and esterified wood with 187.0% WPG (E2).

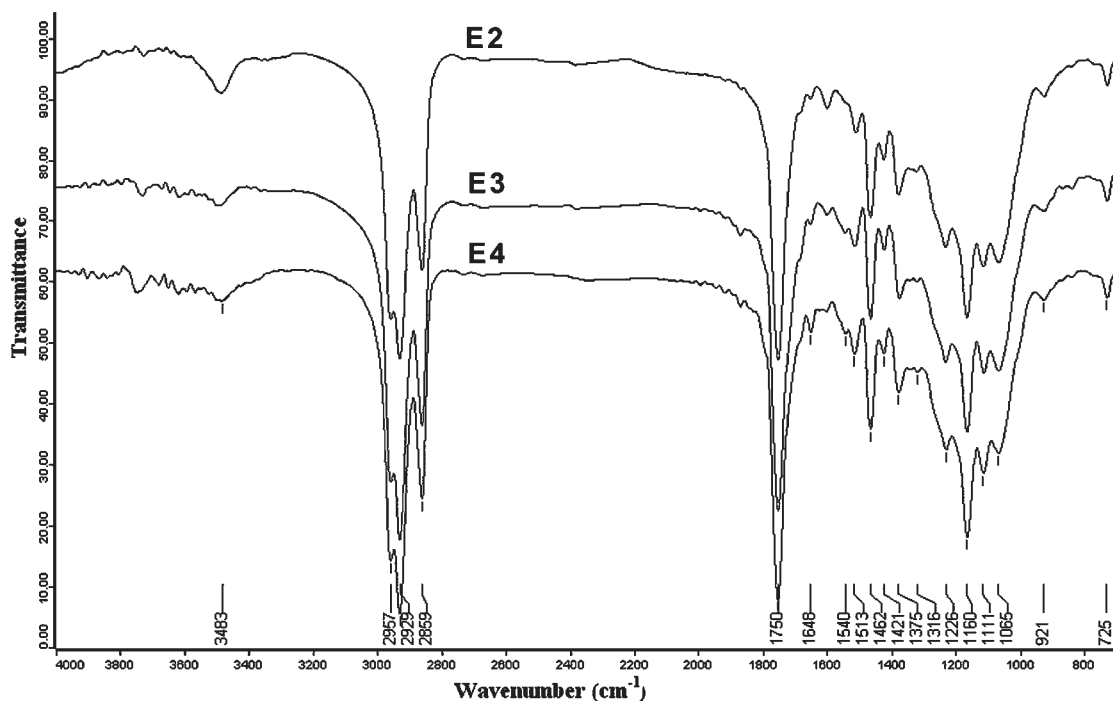


Figure 5. FT-IR spectra of esterified wood with 187.0% WPG (E2); esterified wood with 258.0% WPG (E3); and esterified wood with 297.4% WPG (E4).

esterified wood (E1, E2, E3, and E4) were measured and are compared in Figures 4 and 5. As shown in Figures 4 and 5, after octanoylation, the intensity of the absorption band of OH stretching vibration ($3419\text{--}3484\text{ cm}^{-1}$) was reduced by increasing the molar ratio. Besides, the esterification of wood results in the intensification of the 1750 cm^{-1} peak, due to the new carbonyl groups linked to the wood as esters. The peak at 1160 cm^{-1} (C–O) becomes more intense as new ester groups are formed. The intensity of these two absorptions was significantly increased by increasing the molar ratio. In addition, the intensity of methyl and methylene groups at $3000\text{--}2840\text{ cm}^{-1}$ increased obviously after octanoylation. The C–H symmetrical stretching (ν_s) and asymmetrical stretching (ν_{as}) bands including $2957/2958\text{ cm}^{-1}$

($\nu_s\text{ CH}_3$), 2929 cm^{-1} ($\nu_s\text{ CH}_2$), and $2858/2859\text{ cm}^{-1}$ ($\nu_{as}\text{ CH}_2$) could be clearly distinguished. Meanwhile, the intensities of C–H bending vibrations, such as $1462/1464\text{ cm}^{-1}$ ($\delta_s\text{ CH}_2$), $1375/1377\text{ cm}^{-1}$ ($\delta_s\text{ CH}_3$), and 725 cm^{-1} ($\rho\text{ CH}_2$), were also enhanced.

The infrared analyses of esterified wood were well in accordance with those reported in a previous paper (31). All these analyses confirmed that hydrophobic octanoyl groups replace the hydrophilic hydroxyl groups of wood after octanoylation. However, we must note that the residual OH stretching absorption centered at $3483/3484\text{ cm}^{-1}$ was still existent as a small peak although the molar ratio increased from 1.0 to 2.5. This phenomenon was also observed by Xie et al. (25) when they attempted to acetylate lignocellulosic materials in ionic liquids. They explained

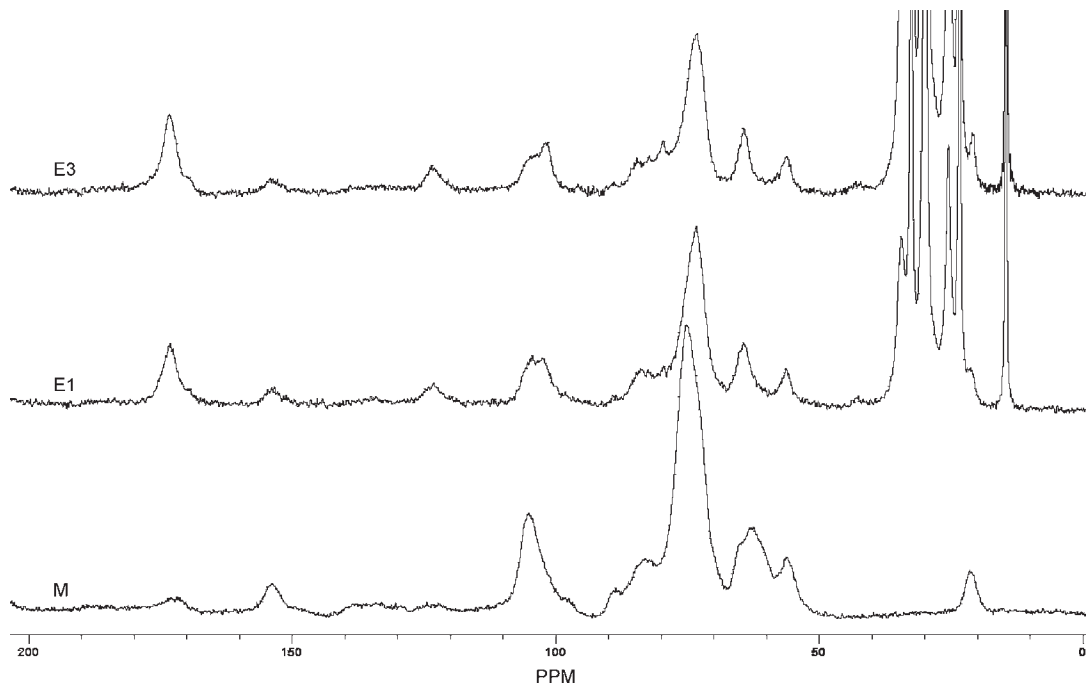


Figure 6. Solid state CP/MAS ^{13}C NMR spectra of wood meal (M, bottom); esterified wood with 121.5% WPG (E1, middle); and esterified wood with 258.0% WPG (E3, top).

that some (albeit minor) phase separation may be taking place when the esterification reagent is added into the wood solution in $[\text{C}_4\text{mim}]\text{Cl}$ causing some OH groups to remain underivatized.

Solid State ^{13}C NMR Analysis. To further investigate the esterification of wood in the ionic liquid homogeneous system, wood meal and esterified wood (E1 and E3) were comparatively studied by ^{13}C NMR CP/MAS (Figure 6). The spectrum for wood meal (Figure 6M) shows a characteristic carbohydrate pattern, namely, C1 (105.0 ppm), C4 (88.5 ppm and 83.0 ppm), and C6 (64.8 ppm and 62.4 ppm). The overlapping signals from C2, C3, and C5 exist as a sharp signal at 75.2 ppm (33). The signals from methoxy groups and methylene groups appear clearly at 56.2 ppm and 21.4 ppm. Besides, a weak signal at 171.9 ppm is typically due to carboxyl groups, which may originate from native aliphatic carboxyl and aliphatic esters. In the spectra of the two esterified woods in Figure 6E1 and E3, the significant differences are the peaks at 14.6, 21.0, 23.4, 25.5, 29.9, 32.5, and 34.5 ppm, all of which belong to the straight-chain alkanes of seven carbons. Furthermore, a sharp signal at 173.2 ppm corresponds to the carbonyl group after esterification.

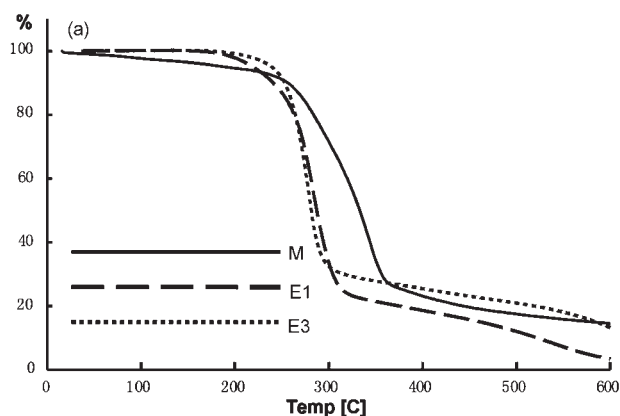
The significant decrease of the intensity of the peak at 88.5 ppm (crystalline C4) and the shifting of peaks of crystalline C6 (64.8 ppm) and amorphous C6 (62.4 ppm) to 64.3 ppm confirmed that cellulose in wood was decrystallized and esterified. Besides, the decrease in the intensity of the signals from C1 and the overlapping signals from C2, C3, and C5 in the spectra of the esterified wood indicated that cellulose and/or hemicelluloses were modified to some extent (34). We could also note that in the spectra of the two esterified woods the signal at 123.1 ppm apparently increased when compared to the corresponding signal of wood meal. This band characteristic of $(\text{Ar})\text{C}-\text{C}$ and its increase indicated that substitution on the aromatic ring of lignin has occurred (35). All above analyses confirmed that the wood meal was octanoylated of the whole component and that the degree of esterification would be enhanced by increasing the amount of the reagent.

TGA/DTG Analysis. Chemically modified wood is utilized in a wide variety of applications, such as fillers for thermoplastics, and

in such applications the thermal stability is a significant issue. In the present study, both TGA and DTG curves of wood meal and esterified wood (E1 and E3) are presented in Figure 7. As can be seen from Figure 7a, there was a small weight loss ($\sim 2.4\%$) from wood meal at $100\text{ }^\circ\text{C}$, which was due to the evaporation of water. However, after homogeneous esterification of the wood in $[\text{C}_4\text{mim}]\text{Cl}$, the weight loss at $100\text{ }^\circ\text{C}$ was zero for the octanoylated wood. This could be explained by the increased hydrophobicity of wood meal after octanoylation as the accessible OH groups in the ionic liquid homogeneous system were replaced by the hydrophobic octanoyl groups. Furthermore, we could note that the amount of carbonized residue at $600\text{ }^\circ\text{C}$ for wood meal, E1, and E3 were 14.5%, 13.2%, and 3.4%, respectively. These results suggested that the octanoyl groups in the octanoylated wood promoted the degradation of the esterified wood and did not contribute to the carbonized residue. The decline of the amount of carbonized residue might also be attributed to the processes of complete dissolution of wood meal and regeneration of esterified wood in $[\text{C}_4\text{mim}]\text{Cl}$.

The rates of the weight loss of the three samples are illustrated in Figure 7b. In the case of wood meal, the different thermo-stability of its main constituents is reflected in the form of two overlapping stages which are registered on the DTG curves (36). The esterified wood, however, exhibited only one stage. It is well known that the DTG_{max} represents the maximum degradation rate and can be used for the comparison of the thermal stability between the samples (37). Obviously, in the present report the DTG_{max} values were found to be $331\text{ }^\circ\text{C}$ for wood meal, $279\text{ }^\circ\text{C}$ for E1, and $285\text{ }^\circ\text{C}$ for E3. Furthermore, the decomposition starting temperature of wood meal, E1, and E3 were found to be about $177\text{ }^\circ\text{C}$, $174\text{ }^\circ\text{C}$, and $156\text{ }^\circ\text{C}$, respectively. These results indicated that octanoylation of wood meal in the $[\text{C}_4\text{mim}]\text{Cl}$ homogeneous system reduced the initial temperature of their thermal degradation and decreased the thermal stability compared to those of unmodified wood meal. However, some previous reports have demonstrated that the thermal stability of wood was improved after octanoylation in a heterogeneous system (31, 38). The differences observed could be due to the

TGA



DrTGA

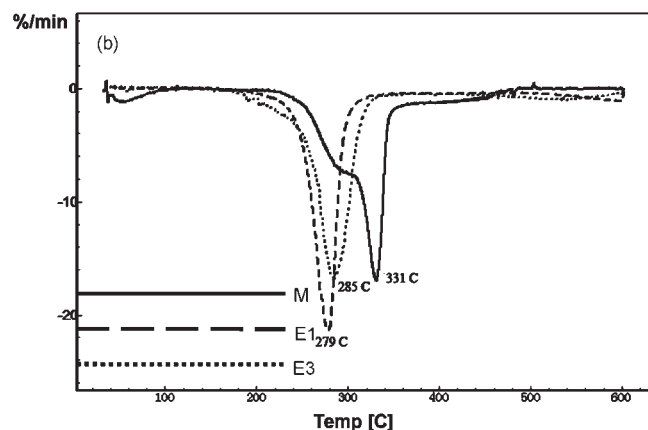


Figure 7. TGA (a) and DTG (b) curves of wood meal (M); esterified wood with 121.5% WPG (E1); and esterified wood with 258.0% WPG (E3).

distinct chemical modification mechanism of wood in the ionic liquid homogeneous system. The complexity of the wood meal was completely transformed into an amorphous structure after regeneration from the esterification system. This explanation has been confirmed by the following XRD and SEM analyses.

XRD Analysis. The major wood component, cellulose, is a highly crystalline polymer of D-anhydroglucopyranose units jointed together in long chains by β -1,4-glycosidic bonds. X-ray analysis of samples of wood sawdust, wood meal, and esterified wood was carried out to demonstrate the decrystallization of cellulose after mild ball-milling, homogeneous modification, and regeneration processes (Figure 8). The data in Figure 8 show that wood sawdust contained two diffraction rays for $2\theta = 22.6^\circ$ and 16.2° (Figure 8S). After mild ball-milling, the first ray due to the 002 plane of the crystal lattice was decreased and shifted to $2\theta = 21.8^\circ$ (Figure 8M). Apparently, the X-ray pattern shows that the crystal region of cellulose disappeared when esterification was conducted in the ionic liquid homogeneous system. The data in Figure 8E1 and E2 illustrate that esterified wood displays a slight broad amorphous diffraction peak centered at $2\theta = 19.8^\circ$. The second ray, at $2\theta = 16.2^\circ$, corresponding to the reflection of planes 101 and $\bar{1}01$ of the native cellulose lattice, disappeared with the appearance of a new peak at $2\theta = 5.1^\circ$. This new peak was attributed to the lateral spaces between the long molecular chains of cellulose produced by functionalization of the glucopyranose rings, which was found by Heritage et al. (39) to depend on the size of the substituent of the hydroxyl groups of cellulose. Similar X-ray diffraction diagrams of esterified wood were also obtained in a heterogeneous

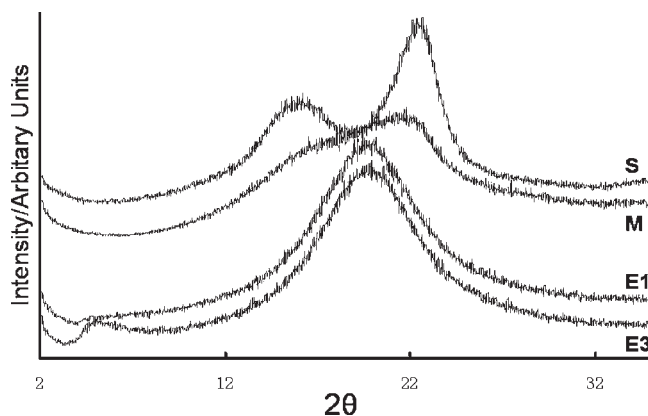


Figure 8. X-ray diffraction diagrams of wood sawdust (S); wood meal (M); esterified wood with 121.5% WPG (E1); and esterified wood with 258.0% WPG (E3).

system (31, 38). These results indicated that the resulting structure of the derivatives is amorphous and that no crystalline regions are present.

SEM Analysis. To better understand how chemical modification affects the morphology of wood meal in the ionic liquid homogeneous system, a series of comparative SEM pictures of wood meal and esterified wood (E1 and E3) are given in Figure 9. The gradual changes of the morphology of the esterified wood were clearly observed with increasing the reagent molar ratio during the reactions. As can be seen from Figure 9, when increasing the molar ratio from 1.0 to 2.0 the fibrillar appearance of wood meal changed into a relatively more homogeneous macrostructure of the esterified wood. Xie et al. (25) have found that the homogeneous chemically modified spruce thermomechanical fibers and spruce sawdust showed a highly porous and considerably more uniform and isotropic structure throughout. In the present study, however, no porous structure has been found. This difference might be due to the different reagents used in the reaction and the degree of esterification. However, the same conclusion we could draw here is that such morphological properties would enhance the compatibility and improve the processability of wood with synthetic polymers.

In summary, the complete dissolution and chemical modification of lignocellulosic with ionic liquids allows the comprehensive utilization of this abundant carbon-neutral renewable resource by combining two major green chemistry principles: using environmentally preferable solvents and sustainable resources. In this article, the homogeneous effective esterification reaction on poplar wood has been carried out in the ionic liquid $[C_4mim]Cl$. The possible mechanism of the homogeneous esterification of wood in $[C_4mim]Cl$ is considered to be similar to that of cellulose, which has been significantly studied. The inaccessible OH groups of the cell wall components in the process of heterogeneous chemical modification would be released and exposed to the system. More OH groups will be involved in the ionic liquid homogeneous chemical modification. Characterization of the esterified wood has proved the high efficiency of homogeneous chemical modification and the potential utilizations of the obtained derivatives.

Although the studies are encouraging, several aspects of this homogeneous chemical modification methodology discussed here need further investigation before they can be considered as an alternative green strategy. First, more efficient ionic liquids should be screened or designed for the fast dissolution of lignocelluloses. In addition, other common reagents for the chemical modification of lignocellulosic should also be investigated in the ionic liquids homogeneous system. The universal laws of the chemical

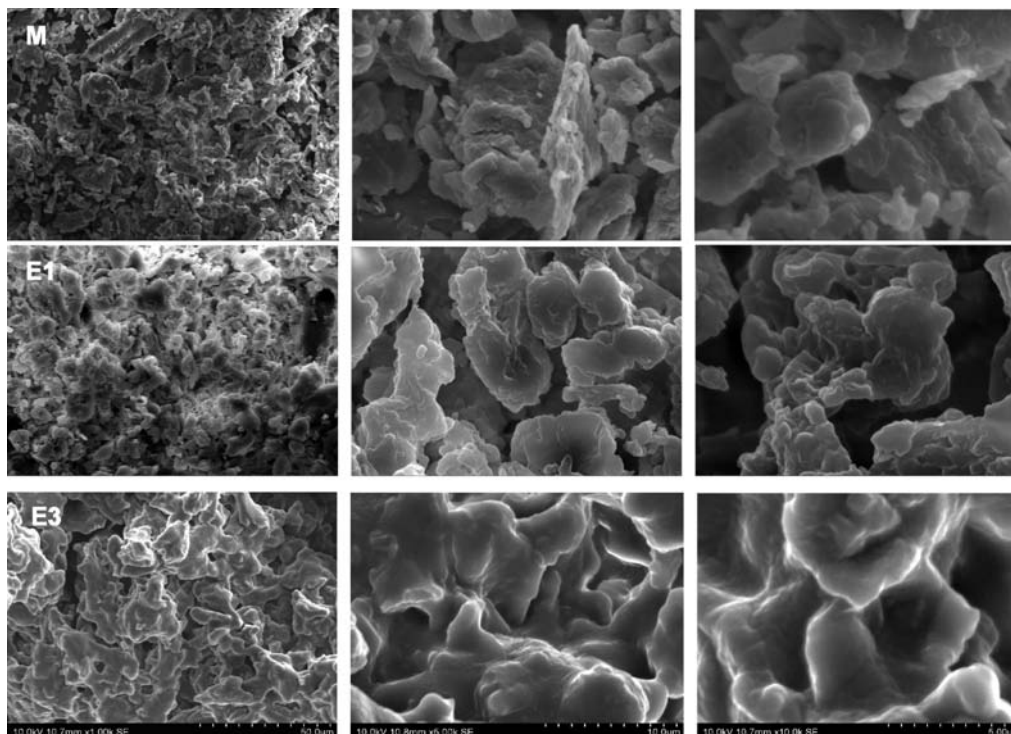


Figure 9. SEM photomicrographs of wood meal (M, top); esterified wood with 121.5% WPG (E1, middle); and esterified wood with 258.0% WPG (E3, bottom).

modification in this homogeneous system should be found. Finally, the practical applications of the derivatives should be studied, such as converting these derivatives into thermoplastic materials.

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Received for review August 5, 2010. Revised manuscript received September 25, 2010. Accepted September 28, 2010. We are grateful for the financial support of this research from the Fundamental Research Funds for the Central Universities (BLYJ200905) and partial funding from Major State Basic Research Projects of China (973-2010CB732204), National Science Foundation of China (30930073), China Ministry of Education (111), State Forestry Administration (200804015, 2010-4-16), and Hei Long Jiang Province for Distinguished Young Scholars (JC200907).