Thorough Chemical Modification of Wood-Based Lignocellulosic Materials in Ionic Liquids

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Homogenous acylation and carbanilation reactions of wood-based lignocellulosic materials have been investigated in ionic liquids. We have found that highly substituted lignocellulosic esters can be obtained under mild conditions (2 h, 70 °C) by reacting wood dissolved in ionic liquids with acetyl chloride, benzoyl chloride, and acetic anhydride in the presence of pyridine. In the absence of pyridine, extensive degradation of the wood components was found to occur. Highly substituted carbanilated lignocellulosic material was also obtained in the absence of base in ionic liquid. These chemical modifications were confirmed by infrared spectroscopy, ^{1}H NMR, and quantitative ^{31}P NMR of the resulting derivatives. The latter technique permitted the degrees of substitution to be determined, which were found to vary between 81% and 95% for acetylation, benzoylation, and carbanilation, accompanied by similarly high gains in weight percent values. Thermogravimetric measurements showed that the resulting materials exhibit different thermal stabilities from those of the starting wood, while differential scanning calorimetry showed discrete new thermal transitions for these derivatives. Scanning electron microscopy showed the complete absence of fibrous characteristics for these derivatives, but instead, a homogeneous porous, powdery appearance was apparent. A number of our reactions were also carried out in completely recycled ionic liquids, verifying their utility for potential applications beyond the laboratory bench.

1. Introduction

Sustainability, industrial ecology, eco-efficiency, and green chemistry are directing the development of the next generation of materials, products, and processes. Biodegradable plastics and biobased composites generated from annually renewable biomass feedstocks are regarded as promising materials that could replace synthetic polymers and reduce global dependence on fossil sources.[1] Polymer blending is a convenient method to develop advanced and novel biocomposites with tailored properties. The chemical, thermal, and physical properties of polymer blends and composites depend on the molecular weight distribution and actual composition of the respective polymers with the miscibility of the individual components being of paramount significance.[2] Many naturally occurring polymers are of hydrophilic nature due to an abundance of hydroxyl or other polar groups. In contrast, a significant number of synthetic commodity polymeric materials are hydrophobic nonpolar materials. In order to increase the miscibility of these hydrophobic materials with various natural polymers, chemical modification and graft polymerization of such polymers are common approaches.[3] Many biodegradable plastics based on polymeric carbohydrates, such as cellulose and starch, have been developed.[4] Despite the significant progress made in this area, the development of economic and abundant alternatives is still a challenge.

Wood is among the most abundant lignocellulosic resources on the planet.[5] Although wood has long been used as a raw material for building, fuel, and various other uses, its potential for conversion to conventional biofuels (e.g., bioethanol) and production of commodity chemicals and biodegradable materials has drawn much attention recently, in view of developments in bioengineering and catalytic chemistry.[6] During the past four decades, the heterogeneous chemical modification of wood has been intensively studied with the aim of improving or modifying its compatibility with thermoplastics, dimensional stability, and resistance to decay. These modifications were always achieved at low efficiency due to the insolubility of the lignocellulosic materials under standard solvation conditions and the use and/or release of environmentally unsustainable reagents, thus limiting potential commercial applications.[7]

Recently, ionic liquids with strong hydrogen bond destroying ability have been developed for the processing of biopolymers.[8] Chemical modification of biopolymers[9] can be carried out, and after reconstitution, biodegradable composites and advanced materials have been obtained.[10] Recently, ionic liquids have been used as solvents for wood preservation and wood liquefaction and for the processing of lignocellulosic materials.[11] In our previous study, we investigated the details of the dissolution of wood-based lignocellulosic materials[12] and have defined the various variables that determine its solubilization efficiency in ionic liquids. In the present paper, we describe our optimization efforts toward the effective homogenous chemical modification of wood in ionic liquids. The resulting materials are shown to be highly substituted with unique and distinctly different morphological and thermal characteristics from those of wood fibers.

2. Experimental Section

2.1. Materials. Ionic liquids, 1-butyl-3-methylimidazolium chloride ([bmim]Cl), 1-allyl-3-methyl-imidazolium chloride ([amim]Cl), and 1-benzyl-3-methylimidazolium chloride ([bnmim]Cl) (Figure 1) were

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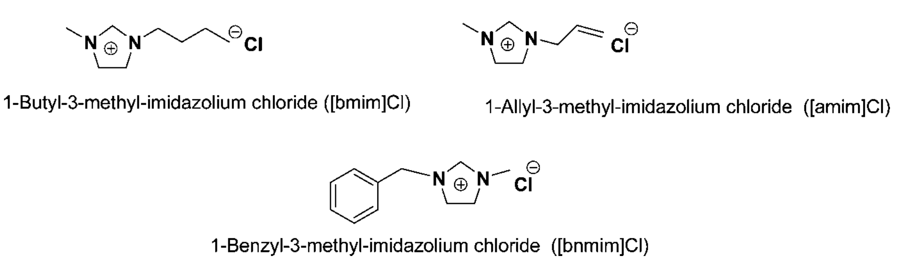


1-Butyl-3-methyl-imidazolium chloride ([bmim]Cl)

1-Allyl-3-methyl-imidazolium chloride ([amim]Cl)

1-Benzyl-3-methyl-imidazolium chloride ([bnmim]Cl)

Figure 1. Ionic liquids used in this study.

synthesized according to literature procedures.[13] Unbleached Norway spruce thermomechanical pulp (TMP) fibers were sampled in a Swedish mill, at 38% dryness, 85 mL Canadian standard freeness of standard newspaper quality. The mill has one-stage refining and a subsequent reject refining (ca. 20%) stage. The pulp was taken at a press stage after the refined and refined reject pulps had been combined. Spruce sawdust was obtained from solid Norway spruce wood, and southern pine TMP was supplied by a southern US company. All wood samples were extracted in a Soxhlet extractor with acetone for 48 h and then kept in a vacuum oven for at least 48 h at 40 °C prior to use. Acetyl chloride, acetic anhydride, benzoyl chloride, and phenyl isocyanate were reagent-grade and used without purification.

2.2. Instruments and Conditions. FTIR spectra were recorded as KBr disks on a Thermo-Nicolet FT-IR spectroscopy. Approximately 10 mg samples were dispersed in a matrix of KBr (300 mg) and pressed to form pellets. All spectra are presented without baseline correction or normalization. Differential scanning calorimetry (DSC) was carried out on 5–10 mg samples using a TA Instrument DSC Q100. The scans were run at a heating rate of 20 °C/min from 20 °C up to 200 °C in an atmosphere of nitrogen. The data from the first scan were discarded since the thermograms often included unwanted thermal history and traces of volatile water. After cooling the sample, the data for a second run were recorded. Thermogravimetric measurements (TGA) were carried out with a TA Instruments TGA Q 500 in the temperature range 25–600 °C, with the temperature being raised at a rate of 10 °C/min. Scanning electron microscopy (SEM) imaging was carried out with a Hitachi S-3200 scanning electron microscope. NMR spectra were acquired using a Bruker 300 MHz spectrometer equipped with a Quad probe dedicated to ^{31}P, ^{13}C, ^{19}F, and ^{1}H acquisition.

2.3. Dissolution of Lignocellulosic Materials in Ionic Liquids. A general procedure for the complete dissolution of wood in ionic liquids is as follows: 4% w/w oven-dried wood TMP fibers were dispersed in a predried ionic liquid solution, and it was stirred at 130 °C for 4–6 h under a N_2 atmosphere.

2.4. Weight Percent Gain (WPG). WPG values were obtained in order to quantitatively follow the modification efficiency of the wood.[14] The as-prepared wood derivative materials were washed, freed of solvent impurities, and dried in a vacuum oven set at 45–50 °C over extended periods of time prior to recording their constant weight. The WPG values reported in this work were calculated according to the formula

$$\text{WPG} \quad (\%) = 100 \times (W_{\text{mod}} - W_{\text{unmod}})/W_{\text{unmod}}$$

where W_{unmod} is the initial oven-dried mass of the lignocellulosic sample before chemical modification and W_{mod} is the oven-dried mass of the modified material. On the basis of our previous work,[15] there are 6.68 mmol/g of aliphatic hydroxyl groups and 1.37 mmol/g of phenolic hydroxyl groups in Norway spruce enzymatic mild acidolysis lignin (EMAL). Independent measurements for this wood showed that it contained 73.4% carbohydrates and 26.6% lignin. As such, one may calculate an approximate value for the total hydroxyl group content in this sample of the examined spruce TMP (15.7 mmol/g). From these data, one may then calculate a theoretical WPG value for each modification reaction performed.

2.5. Typical Acylation of Lignocellulosic Materials in Ionic Liquids. Pyridine (0.55 mL, 7.55 mmol) was added to a wood solution (6 g, containing 4% w/w spruce ionic liquid [bmim]Cl solution), followed by incremental addition of benzoyl chloride (0.88 mL, 7.55 mmol, 2 mol mol $^{-1}$ hydroxyl groups in wood). This solution was initially stirred at room temperature for 10 min and then kept at 70 °C for 2 h. Isolation of the derivative was carried out by precipitation of the cooled solution into methanol (100 mL), followed by water (100 mL) under rapid agitation. The solid product was obtained after filtration and washing with methanol/water (1/1, v/v mixture). The product with a fluffy, powdery texture (0.58 g) was obtained after being vacuum-dried at 40 °C for 18 h; WPG = 143% (max. theoretical WPG = 164%).

2.6. Typical carbanilation of Lignocellulosic Materials with Phenyl Isocyanate in Ionic Liquids. Phenyl isocyanate (0.82 mL, 7.55 mmol, 2 mol mol $^{-1}$ hydroxyl groups in wood) was carefully added into a wood solution (6 g, 4% w/w in ionic liquid [bmim]Cl). This was stirred at room temperature for 10 min and then kept at 70 °C for 2 h. Product isolation was carried out by using the same method as for the acylation process. The product was obtained after filtration and washing with methanol/water (1/1, v/v mixture). The product, a white solid powder (0.58 g), was obtained after being dried in a vacuum oven set at 40 °C for 18 h; WPG = 142% (max. theoretical WPG = 187%).

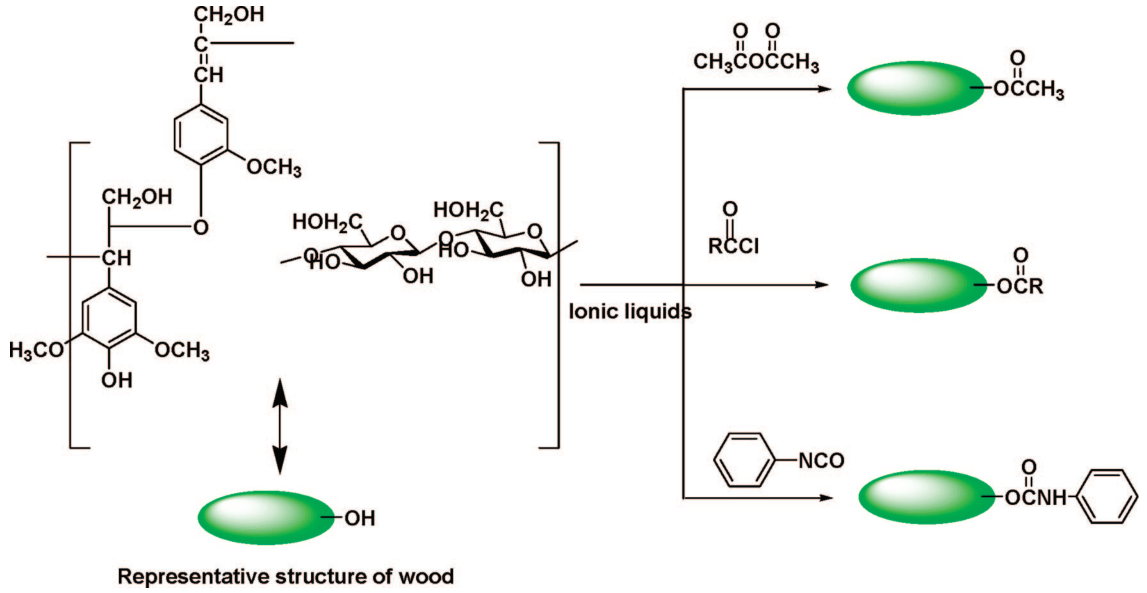
2.7. Typical Quantitative ^{31}P Nuclear Magnetic Resonance Analysis of Wood-Based Derivatives. The ionic liquid, [amim]Cl, was used as the solvent for quantitative ^{31}P NMR analyses. A complete description of the method development will be published elsewhere.[16] A typical procedure was as follows: Lignocellulosic sample or wood derivative (20 mg) was accurately weighed into a 5 mL sample bottle. 1-Allyl-3-methylimidazolium chloride (1 g) was then added and the mixture stirred at 120 °C for 5 h. Pyridine-D_5 (300 μL), internal standard solution (100 μL, 0.1212 mol/L, *endo-N*-hydroxy-5-norbornene-2,3-dicarboximide in Py-D_5/$CDCl_3$ = 1.6/1, v/v), and $Cr(acac)_3$ (25 μL, 0.0312 mol/L) used as relaxation reagent were also added followed by phosphatylating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, 200 μL). NMR acquisition ensued 10–20 min after the final addition using typical spectral acquisition conditions that have been described elsewhere.[17]

2.8. Determination of Percentage DS Values of Wood Derivatives. The percentage DS (%DS) of selected wood derivative was determined by quantitative ^{31}P-NMR analysis. This may be calculated by using the following equation, supposing the mass of the wood is regenerated completely as derivative

$$\text{DS} = 100 \times \{1 - [(M_{\text{PRODUCT}} \times C_{\text{PRODUCT-OH}})/(M_{\text{WOOD}} \times C_{\text{WOOD-OH}})]\} \quad (1)$$

where M_{PRODUCT} is the dried mass of the recovered product and M_{WOOD} is the mass of the original dried wood; $C_{\text{PRODUCT-OH}}$ is the amount of hydroxyl groups per gram in the recovered product and $C_{\text{WOOD-OH}}$ is the amount of hydroxyl groups in the original wood sample, as determined by ^{31}P NMR analysis. In this respect, it is even easier to determine %DS based on the WPG values alone. However, in most cases it is reasonable to assume that there is some loss of products or presence of byproducts that can add significant error to this calculation. As most reactions are likely to have yields less than 100% or produce products containing impurity, a more refined interpretation of the results is required on the basis of the integrati

Scheme 1. Representative Structures of Wood Components and the Homogenous Functionalization Reactions Carried out in Ionic Liquids



of the ^{31}P NMR internal standard vs the remaining lignocellulose hydroxyl integrations and a representation of the values in moles per gram of isolated product. Due to the increased molecular weight of the macromolecules upon substitution, one may calculate values for the available hydroxyl groups, after derivatization, per gram of wood substrate and %DS based on ^{31}P NMR of a weighed sample of product using the following equations:

$$\mathrm{OH_{SUB}} = [(\mathrm{OH_{TH}}/\mathrm{OH_{OBS}}) - 1]/[\mathrm{Frag_{MW}} + (1/\mathrm{OH_{OBS}})] \quad (2)$$

$$\%\mathrm{DS} = 100 \times \mathrm{OH_{OBS}}/\mathrm{OH_{TH}} \quad (3)$$

where $\mathrm{OH_{OBS}}$ is the observed value from phosphitylation in moles per gram, as determined by the ^{31}P NMR ratios of internal standard vs lignocellulose hydroxyl integrations, for a weighed sample. $\mathrm{OH_{TH}}$ is the maximum phosphitylation value obtainable in moles per gram of underivatized lignocellulose, as determined by complete phosphitylation and analysis by ^{31}P NMR of the native substrate. $\mathrm{Frag_{MW}}$ is the molecular weight of the substituent fragment, not including the attaching oxygen atoms from the native substrate. $\mathrm{OH_{SUB}}$ is the theoretical value for derivatized hydroxyls in moles per gram of underivatized lignocellulose, based on the assumption that there is no change in molecular weight upon derivatization.

Table 1. Acetylation Conditions Examined for the Derivatization of Wood-Based Lignocellulosic Material in Ionic Liquids[a]

no.	ionic liquids	molar ratio[b]	reagent	temp (°C)	reaction time (h)	WPG (%)
A1[c]	[bmim]Cl	2	Ac_2O	70	3	–30
A2	[bmim]Cl	2	Ac_2O	70	3	50
A4[c]	[bmim]Cl	2	AcCl	70	2	20
A3	[bmim]Cl	2	Ac_2O	70	10	34
A5	[bmim]Cl	2	AcCl	70	3	58
A6	[bmim]Cl	2	AcCl	70	1	54
A7	[bmim]Cl	2	AcCl	70	2	65
A8	[bmim]Cl	2	AcCl	70	10	48
A9	[bmim]Cl	2	AcCl	80	2	63
A10	[bmim]Cl	1.5	AcCl	70	2	35
A11	[bmim]Cl	2.5	AcCl	70	2	64
A12	[bnmim]Cl	2	AcCl	70	2	63
A13	[amim]Cl	2	AcCl	70	2	63
A14	[bmim]Cl	2	AcCl	70	2	64
A15[d]	[bmim]Cl	2	AcCl	70	2	71
A16[e]	[bmim]Cl	2	AcCl	70	2	40
A17[f]	[bmim]Cl	2	AcCl	70	2	63

[a] Using spruce TMP as model lignocelluosic material unless otherwise specified. [b] Molar ratio of acetylation reagent and pyridine to hydroxyl groups in the lignocellulosic material (based on 13.3 mmol/g of hydroxyl groups present in wood as determined by quantitative ^{31}P NMR). [c] In the absence of pyridine. [d] Using pine TMP as original lignocellulosic materials. [e] Using neat methanol as solvent to precipitate the product. [f] Using recycled ionic liquid [bmim]Cl as the solvent medium.

2.9. Recycling and Purification of Ionic Liquids from the Wood Acetylation Reaction. Na_2CO_3 aqueous solution (20 wt %) was added slowly into the ionic liquid/water/methanol solution that resulted from a typical acetylation run as described previously until the pH of the mixed solution reached 9.0. Any possible precipitate was filtered, and water and methanol were removed using a rotary evaporator. Dichloromethane (20 mL) was then added into the residue, and then the solution was dried with anhydrous Na_2SO_4 for 2 h. The dried material was then filtered. 5.4 g of recycled ionic liquid was obtained (yield 94%), vacuum drying for 24 h at 70 °C.

3. Results and Discussion

3.1. Acylation of Wood in Ionic Liquids. During our efforts to improve the compatibility of lignocellulosic materials with nonpolar thermoplastics, we applied a variety of reactions aimed at chemically modifying wood as described in Scheme 1. Carboxylic acid anhydrides, acid chlorides, and isocyanates were reagents examined, due to their high reactivity toward the hydroxyl groups of the wood cell-wall polymers.[18] Initially, we investigated the acetylation and benzoylation reactions of wood dissolved in ILs using acetyl chloride (AcCl), acetic anhydride (Ac_2O), and benzoyl chloride. When using acetic anhydride and/or acetyl chloride as acylation reagents in the absence of pyridine, significant degradation accompanied the reaction as evidenced by the low weight percent gain (WPG) values obtained (Table 1, entry A1). Surprisingly, this is in contrast to a previous report on the acylation of cellulose under similar conditions where high yields with high degrees of substitution were reported.[19] Perhaps the presence of lignin in wood may account for the differences. The addition of pyridine, which is known to act as an acid acceptor in such systems, was found to increase the WPG values very significantly (by about 80%). Over a period of 3 h and under otherwise identical conditions, the WPG value was 50% (Table 1, entry A2), which is close to the theoretically calculated value of 66% (based on 13.3 mmol/g of hydroxyl groups present in wood as determined by quantitative ^{31}P NMR). Increasing the reaction time did not lead to higher yields, possibly due to partial degradation caused by the presence of the Brφnsted acidic pyridinium acetate formed (Table 1, entry A3). As anticipated and under similar conditions, acetyl chloride was found to be a more reactive acylation reagent than acetic anhydride. This is evidenced by the higher WPG value of 58% (Table 1, entries A2, A5) obtained for it, which is significantly greater than that (34%) obtained when acetic anhydride was used (Table 1, entries A2, A3). When using acetic anhydride, prolonging the reaction time to over 2 h had no beneficial effects, since a slight decrease in the yield was observed. This was possibly due to degradation and/or partial deacetylation reactions taking place during the workup of the samples in the presence of the Brφnsted acidic pyridine hydrochloride formed (Table 1, entries A6, A7, A8), which is consistent with similar published data that dealt with the acetylation of cellulose in ionic liquid media.[20]

An examination of the effect of the reaction temperature, time, and the required excess of derivatizing reagent was also carried out. On the basis of WPG data, for entries A7 and A9–11 (Table 1), one arrives at the conclusion that the optimal conditions are met under a molar ratio of 2/1 (reagent/substrate), 2 h reaction time, and about 70 °C. Increasing the temperature beyond 70 °C was found to cause product degradation, while increasing the molar ratio of reagent/substrate beyond 2 did not show any additional significant increase in the yields. By altering the nature of the cation of the ionic liquid (entries A12–14), and under otherwise identical conditions, similar WPG values were obtained. Similar data were also obtained when a completely recycled ionic liquid was used (entry A17, Table 1).

The effect of the nature of wood on its reactivity was also examined. Whether spruce sawdust or spruce TMP fibers were used, these samples showed similar reactivity when dissolved in [bmim]Cl, under otherwise identical conditions (entries A7 and A14–15; Table 1). This is not surprising, since the dissolution of a wood sample, from the same source, results in a completely homogeneous mixture when dissolved in ionic liquid media.[12] However, when the acetylation reaction was carried out on pine TMP fibers (entry A15, Table 1), under otherwise identical conditions to those previously enumerated, a somewhat higher WPG value was obtained.

It is important to note at this point that existing commercial processes used for the heterogeneous acetylation of wood, using acetic anhydride as the acetylating agent, result in WPG values that are less than 25%.[18] The homogeneous acetylation process offered by ionic liquids apparently offers products of considerably higher WPGs with high degrees of substitution (DS), as shown in section 3.4 of this paper. When neat methanol was used as the nonsolvent to precipitate the product after the reaction, a significantly decreased yield was observed, as evidenced by the WPG value of 40% (entry A16, Table 1). Using methanol/water (1:1) as the precipitation medium resulted in a WPG value of 65% (entry A7, Table 1). It is likely that some acetylated wood components are partially soluble in neat methanol causing the reduction in the observed yield. The nature of these components is currently under examination to further understand and possibly capitalize on the fractionation opportunities thus presented.

Among the various attractive features of ionic liquids is their recycling ability. Consequently, we investigated the efficiency of the wood acetylation reaction and have compared the proton NMR spectra of recycled [bimim]Cl ionic liquid with a fresh sample (Supporting Information Figure S1). Overall, the recycling potential of [bmim]Cl in terms of the presented proton spectra, its wood solubilization efficiency, and the course of the acetylation reaction (Table 1, entry A17), was found to be rather satisfactory. Once removal of excess water, excess reagents, and pyridine hydrochloride has occurred, the resulting ionic liquid can be recycled.

Table 2. Acylation Conditions Examined for the Derivatization of Spruce TMP with Benzoyl Chloride in the Presence of Pyridine in [bmim]Cl

no.	molar ratio[a]	temp (°C)	reaction time (h)	WPG (%)
B1	2	70	2	143
B2	2	70	3	150
B3	2	80	2	140
B4	2	80	11	108
B5[b]	2	70	2	84
B6[b]	2.5	70	2	92

[a] The molar ratio of PhCOCl and pyridine to hydroxyl groups in spruce TMP (based on 13.3 mmol/g of hydroxyl groups present in wood as determined by quantitative ^{31}P NMR). [b] Using pure methanol as solvent to precipitate the product.

Table 3. Carbanilation Conditions Examined for the Derivatization of Spruce TMP in Ionic Liquid [bmim]Cl Using Phenyl Isocyanate

no.	molar ratio[a]	temp (°C)	reaction time (h)	WPG (%)
C1	2	70	2	142
C2	1.5	70	2	123
C3	2.5	70	2	145
C4	2	70	8	150
C5	2	70	24	165
C6	2	80	2	152

[a] The molar ratio of PhNCO to hydroxyl groups in spruce TMP (based on 13.3 mmol/g of hydroxyl groups present in wood as determined by quantitative ^{31}P NMR).

Hon et al. have demonstrated that the introduction of phenyl groups onto wood results in an increase in its compatibility with polystyrene.[21] We examined the acylation of spruce TMP fibers with benzoyl chloride. For this set of experiments, high WPG values were obtained (Table 2, entries B1, B2) which were rather close to the theoretical WPG of 164%. In a manner similar to the acetylation reaction already discussed, increasing the reaction temperature was found to lead to lower yields. A slight increase in the reaction time was found to increase the yield (entries B3 and B2, Table 2), but further extending it (entry B4, Table 2) and elevating the reaction temperature (entry B4, Table 2) was found to cause a decrease in the WPG. This increase in WPG observed by increasing the reaction time from 2 to 3 h (entries B3 and B2, Table 2) may be due to the lower reactivity of the benzoyl chloride compared to acetyl chloride and/or the lower reagent mass transfer considerations occurring with benzoyl chloride. In a manner similar to the acetylation reaction, the use of methanol as a precipitation medium resulted in significantly lower yields of benzoylated wood (entries B5 and B6, Table 2).

3.2. Carbanilation of Wood in Ionic Liquids. Phenyl isocyanate was used, as a “neutral” reagent, for the purpose of wood modification (Table 3). Previous literature accounts have referred to this reaction being carried out on cellulose in ionic liquids.[22] However, there have been no accounts of this reaction being carried out on lignocellulosic materials in ionic liquids. Highly substituted carbanilated lignocellulosic materials were obtained under relatively short reaction periods (2 h) and with the use of a low molar ratio of isocyanate to hydroxyl groups in wood (entries C1, C4, C5, C6; Table 3). Our data indicate that the WPG values increase with increasing molar ratio of isocyanate to wood OH groups. For example, a ratio of 1.5 mol of phenyl isocyanate per mole of wood hydroxyl groups resulted in a WPG value of 123% (entry C2, Table 3), which increased to 142% when the molar ratio was increased to 2 (entry

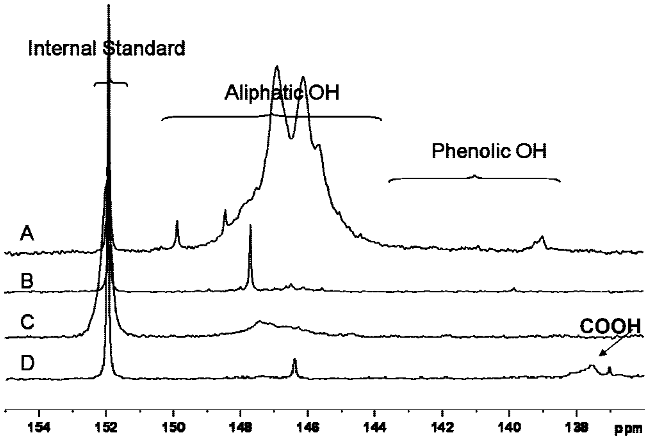


Figure 2. Comparative ^{31}P NMR spectra of spruce and spruce derivatives. (A) Spruce TMP. (B) Carbanilated spruce with 165% WPG value (entry C5, Table 3). (C) Benzoylated spruce with 150% WPG value (entry B2, Table 2). (D) Acetylated spruce with 65% WPG (entry A7, Table 1). The sharp signals at 147.6, 148.2, and 149.8 ppm are artifacts (see text).

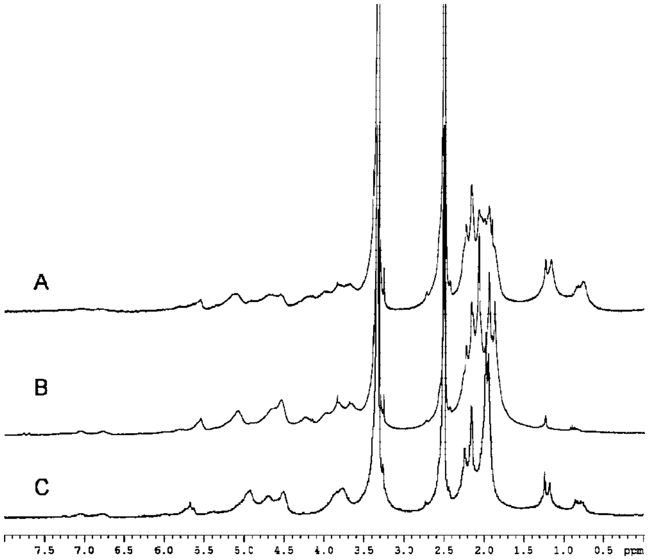


Figure 3. ^1H NMR (DMSO-d_6) spectra of (A) methanol-soluble fraction of acetylated spruce product, (B) acetylated cellulose, and (C) Acetylated xylan.

Table 3). In a manner similar to our findings for the acylation reactions, further increase in the molar ratio of isocyante/wood OH groups to 2.5 caused only a minor increase in the WPG value (entry C3, Table 3). Increases in the reaction temperature and time also resulted in slight increases in WPG. For example, prolonging the reaction time from 2 to 24 h (entries C2, C4, C5; Table 3) increased the WPG value by 11%, while an increase of 8% was observed by raising the temperature from 70 to 80 °C (entries C1 and C6, Table 3).

Overall, the data of Table 3 show that the optimum reaction conditions for the carbanilation of spruce wood are distinct from those derived for its acetylation. Apparently, the optimized WPG value of 165%, for the carbanilation of spruce wood (entry C5, Table 3), is somewhat further from its theoretical value of 187% compared to the optimized WPG value for acetylation and its theoretical counterpart (see Table 1). This may demonstrate that the uncatalyzed phenyl isocyanate reaction on spruce wood is less efficient, as compared to its acetylation.

3.3. Infrared Spectroscopy Study of Wood Derivatives. The formation of ester and urethane linkages by the various hydroxyl groups in wood was evident in the IR spectra of the derivatives (Supporting Information Figures S2–S4). A significant decrease in the broad region responsible for OH stretching vibrations, centered at 3416 cm^{-1}, was apparent in all derivatives (Supporting Information Figures S2–S4). This decrease was accompanied by a significant increase in the absorption at around 1726–1752 cm^{-1} characteristic of the −CO stretching bands for all derivatives (Supporting Information Figures S2–S4). Furthermore, as anticipated, the band at 1230 cm^{-1}, characteristic of the COC ester stretching bands, was also significantly increased in all derivatives (Supporting Information Figures S2–S4). For the case of carbanilated wood derivatives, characteristic absorptions at 1731, 1221, and 754 cm^{-1} due to the C=O and C—N stretching bands for the carbamate groups were apparent (Supporting Information Figure S4). The N—H stretching band for this derivative was found to be 3990 cm^{-1}, which contributed to the broad residual band centered at 3400 cm^{-1}.

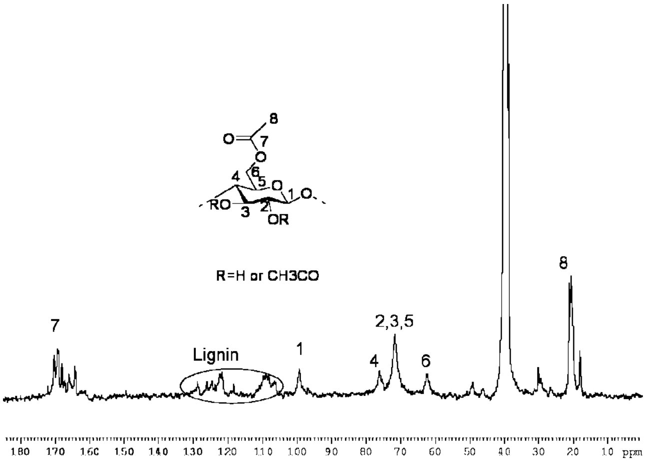


Figure 4. ^{13}C NMR spectrum (DMSO-d_6) of methanol-soluble fraction of acetylated spruce product.

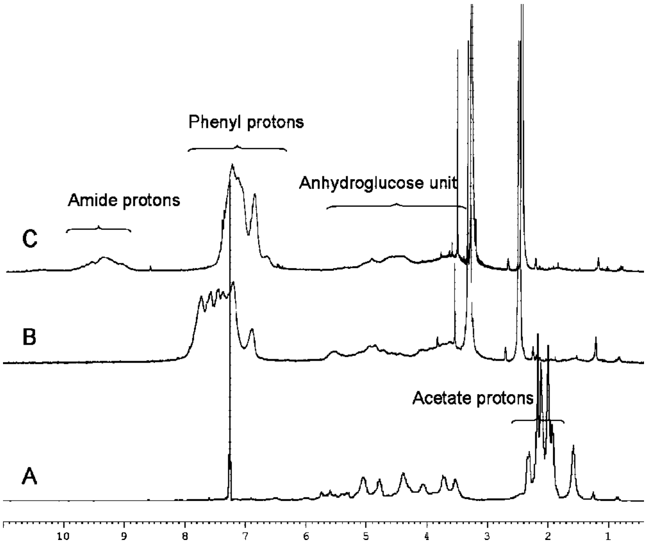


Figure 5. ^1H NMR spectra of (A) acetylated spruce TMP (entry A7, Table 1) with 65% WPG, 92.6% DS, in chloroform-d); (B) benzoylated spruce TMP (entry B2, Table 2) with 150% WPG, 94.0% DS in DMSO-d_6; (C) carbanilated spruce TMP (entry C5, Table 3) with 165% WPG, 89.7% DS in DMSO-d_6).

In an effort to understand why the residual OH stretching absorption centered at 3416 cm^{-1} was still apparent in all our IR spectra, we attempted to completely acetylate (using acetyl and benzyl chlorides) and carbanilate pure cellulose for periods of time extending up to 10 h. While the intensity of the

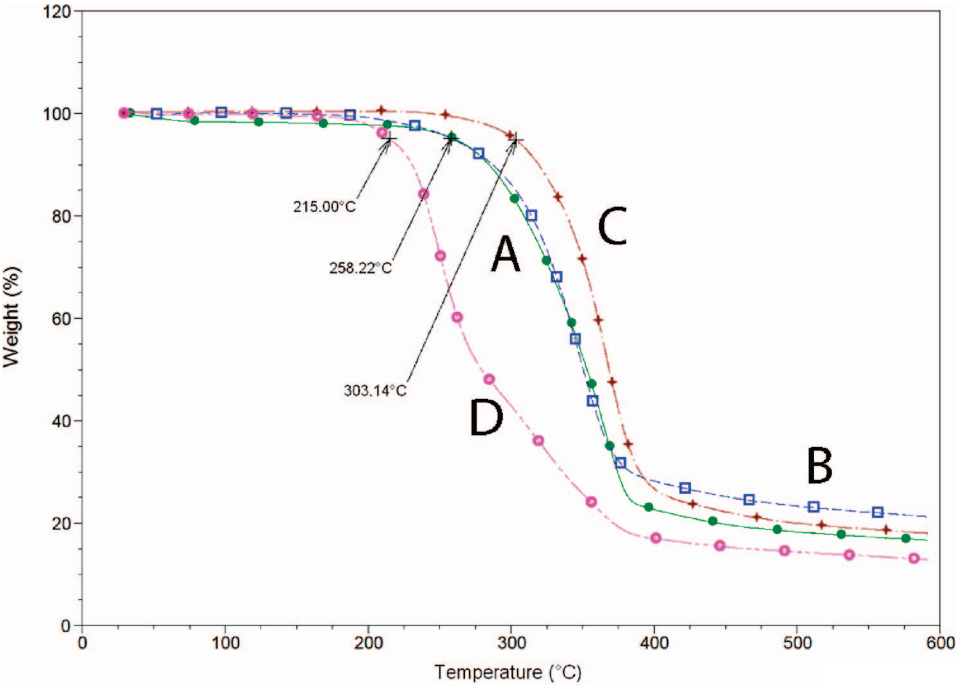


Figure 6. Comparison of the thermogravimetric analysis data for different modified spruce samples: (A) spruce TMP; (B) acetylated spruce with 65% WPG (entry A7, Table 1) of DS = 92.6%; (C) benzoylated spruce with 150% WPG (entry B2, Table 2) with a DS of 94.0%; (D) carbanilated spruce with 165% WPG (entry C5, Table 3) with a DS of 89.7%.

Table 4. Degree of Substitution (DS) Values for Wood Derivatives[a]

wood derivatives	A2	A7	A15	B2	B5	B6	C2	C5
WPG (%)	50	65	71	150	84	92	123	165
DS values (%)	92.8	92.6	94.4	94.0	91.3	91.0	81.0	89.7

[a] Based on quantitative ^{31}P NMR OH group determinations (starting wood contained 13.3 mmol/g of hydroxyl groups).

absorption band at 3416 cm^{-1} in all cases decreased with increasing reaction time, it was never totally eliminated. Incremental and extremely slow (1–2 mL/h) addition of acetic anhydride during the acetylation of wood, however, successfully completely eliminated the aforementioned OH absorption band.[12] This most likely indicates that some (albeit minor) phase separation may be taking place when the acylation or carbanilation reagents are added into the wood solution in [bmim]Cl causing some OH groups to remain underivatized.

3.4. Quantitative ^{31}P NMR Studies of Wood Derivatives. The use of quantitative ^{31}P NMR has proven to be a useful tool to qualitatively and quantitatively evaluate the various hydroxyl groups present in lignin.[17] Despite that fact that the wood derivatives, obtained during this work, were only partially soluble in traditional solvents, they were completely soluble in ionic liquids such as [amim]Cl and [bmim]Cl. Quantitative ^{31}P NMR spectra of spruce and spruce derivatives were, therefore, obtained (Figure 2) using ionic liquids as cosolvents (see Experimental Section and ref 16).

The quantitative ^{31}P NMR data from the starting spruce TMP wood (Figure 2A) show the presence of 13.3 mmol/g hydroxyl groups. This value is close to the theoretically calculated value of 15.7 mmol/g (see section 2.4).

The broad chemical shift area ranging between 144 and 149 ppm is known to be responsible for the phosphitylated OH groups that belong to the various carbohydrate and lignin aliphatic OH groups present in unmodified spruce TMP (Figure 2A). A satisfactory reduction of the absorption intensity in both aliphatic OH groups and phenolic OH value is apparent in all the ^{31}P NMR spectra of the derivatives depicted in Figure 2B, 2C, and 2D. This is a testament to the pronounced reactivity of the hydroxyl groups in cellulose, hemicellulose, and lignin. The sharp signals at 147.6 ppm in Figure 2B and 148.2 ppm and 149.8 ppm in Figure 2A are artifacts caused by some non-wood-related species of yet unknown origin. With the quantitative spectral information from Figure 2, the degree of substitution values (DS) for all wood derivatives were obtained using eqs 1 and 2 (see section 2.8).

The DS value of acetylated spruce having a WPG value of 65% (theoretical 66%) was 92.6%, while that of benzoylated spruce with a WPG of 150% (theoretical WPG 164%) was 94.0%. Finally, carbanilated spruce TMP with a WPG of 165% (theoretical WPG 187%) showed a DS of 89.7%. These data demonstrated that highly substituted lignocellulosic materials were obtained. It is also of interest to note that the DS values for benzoylated spruce (entries B5 and B6, Table 2) were found to be in excess of 90%. These materials showed low WPG values, since they were precipitated from methanol.

On the basis of data presented in Figure 2, one may conclude that the phenolic hydroxyls from the lignin component in wood have been completely derivatized, due to the absence of phosphitylated phenolic peaks in the ^{31}P NMR spectra (B, C, and D). It is also obvious that the native carboxylates associated with lignin and/or the hemicelluloses in wood have been completely derivatized. Sample D is exceptional in the fact that the acetyl anhydrides may have hydrolyzed during workup, due to different workup conditions, morphologies of the products, or increased hydrophilicity, in comparison to the extensively benzoylated or aryl carbanilated samples. However, due to the complex nature of the interactions and the structure of wood, the observation of complete functionalization of phenolics hydroxyl groups within lignin does not provide enough evidence to indicate the selective derivatization of one biomacromolecule type over another. This issue is extensively discussed in ref[16]

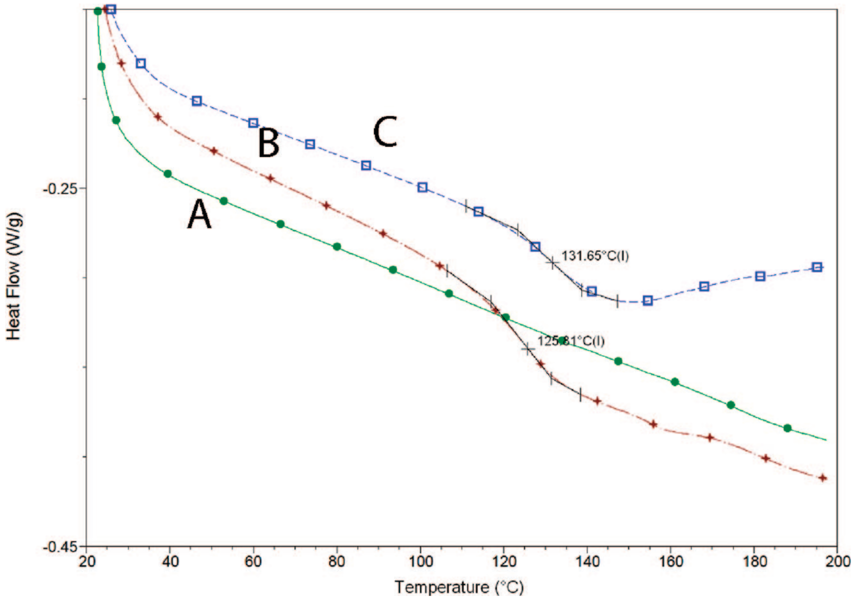


Figure 7. DSC analysis of wood derivatives: (A) spruce TMP; (B) benzoylated spruce with 150% WPG (entry B2, Table 2) with a DS of 94.0%; (C) acetylated spruce with 65% WPG (entryA7, Table 1) with a DS of 92.6%.

3.5. ^{1}H NMR and ^{13}C NMR Spectra of Wood Derivatives. Since the use of neat methanol as a precipitation medium after wood acetylation with acetyl chloride resulted in significantly lower WPG values, some material losses due to solubilization were evident. These soluble products were precipitated by adding an equal volume of water into the filtrate methanol. The precipitated material was found to have good solubility in $CHCl_3$, DMSO, and other organic solvents. Consequently, it became possible to attempt their structural elucidation using ^{1}H NMR and ^{13}C NMR spectroscopy.

The ^{1}H NMR spectrum of the methanol-soluble product is shown in Figure 3. For comparative purposes, the ^{1}H NMR spectra of acetylated cellulose and acetylated xylan prepared under identical conditions are also shown. The similarities among these three spectra are evident, signifying that the isolated methanol soluble material is rich in carbohydrates. The ^{13}C NMR spectrum of the same methanol soluble material is in Figure 4; when coupled with the ^{1}H NMR data of Figure 3, it supplies strong evidence that the methanol-soluble material is mainly cellulose acetate whose signal assignment is shown in Figure 3. For example, the downfield signals at $\delta = 162.0–171.0$ ppm are characteristic of carbonyl carbons; those at $\delta = 62.0–99.4$ ppm are due to the cellulose backbone and at the signal $\delta = 21.2$ ppm are due to the acetate methyl carbons. However, the signals at $\delta = 106.0–130.0$ ppm also show the presence of minor traces of aromatic residues most likely due to lignin.

To further probe the structure of the obtained acetylated, benzoylated, and carbanilated wood derivatives, the ^{1}H NMR spectra of these materials that displayed the highest WPG values were obtained in deuterated chloroform or DMSO-d_6 (Figure 5). The appearance of a large acetate $-CH_3$ signal is apparent in Figure 5A, which demonstrates the high DS of acetylation on spruce wood. Similarly, the appearance of large phenyl proton resonances compared to the anhydroglucose units in the ^{1}H NMR of benzoylated (Figure 5B) and carbanilated spruce (Figure 5C) demonstrates that highly substituted lignocellulosic materials have been obtained.

3.6. Thermal Analysis of Wood and Wood Derivatives. The thermal properties of the obtained derivatives are of significance as far the eventual utilization of such materials is concerned. As can be seen from Figure 6, the thermal stability of spruce derivatives varies with the structure of the modifying reagent. For example, the acetylated spruce (entry A7, Table 1) that showed a DS of 92.6% (Table 4) shows a similar thermal stability to the original spruce TMP that starts to decompose at 190 °C (Figure 6A). As anticipated, the presence of an aromatic group in the wood structure as in the case of benzoylated spruce (entry B2, Table 2), with a DS of 94.0%, showed a higher thermal stability and decomposition temperature (around 220 °C) than that of acetylated wood. Although the carbanilated spruce (entry C5, Table 3) with a DS of 89.7% was found to start decomposing at near 190 °C (Figure 6D), its decomposition is seen to be much steeper than either the acetylated (Figure 6B) or benzoylated (Figure 6C) spruce. For example, for a 5% weight loss, a temperature of about 258 °C was required for spruce TMP, while for acetylated and carabanilated spruce, temperatures of 215 and 303 °C were required, respectively.

The various thermal transitions apparent in the synthesized materials were examined using differential scanning calorimetry (DSC) (Figure 7). Such measurements can be used to investigate the presence or absence of intermolecular interactions among the various components. Qualitative indications in relation to the extent of disruption of hydrogen bonding may also be obtained. Figure 7A shows the DSC thermogram of the original spruce TMP. As anticipated, this sample does not show any notable transition, mostly due to the presence of an extensive hydrogen bonded network structure, whose disruption usually leads to thermal decomposition rather that to a transition.[23] However, the efficient, homogeneous derivatization of wood in ionic liquids provided an ideal environment for the production of uniformly substituted new materials that showed various distinct thermal transitions occurring below their decomposition temperatures. Clear glass transition temperatures (T_g) were apparent for acetylated (131.7 °C) and benzoylated (125.8 °C) wood. The actual minor reduction in the T_g between these two can readily be rationalized on the basis of the free volume

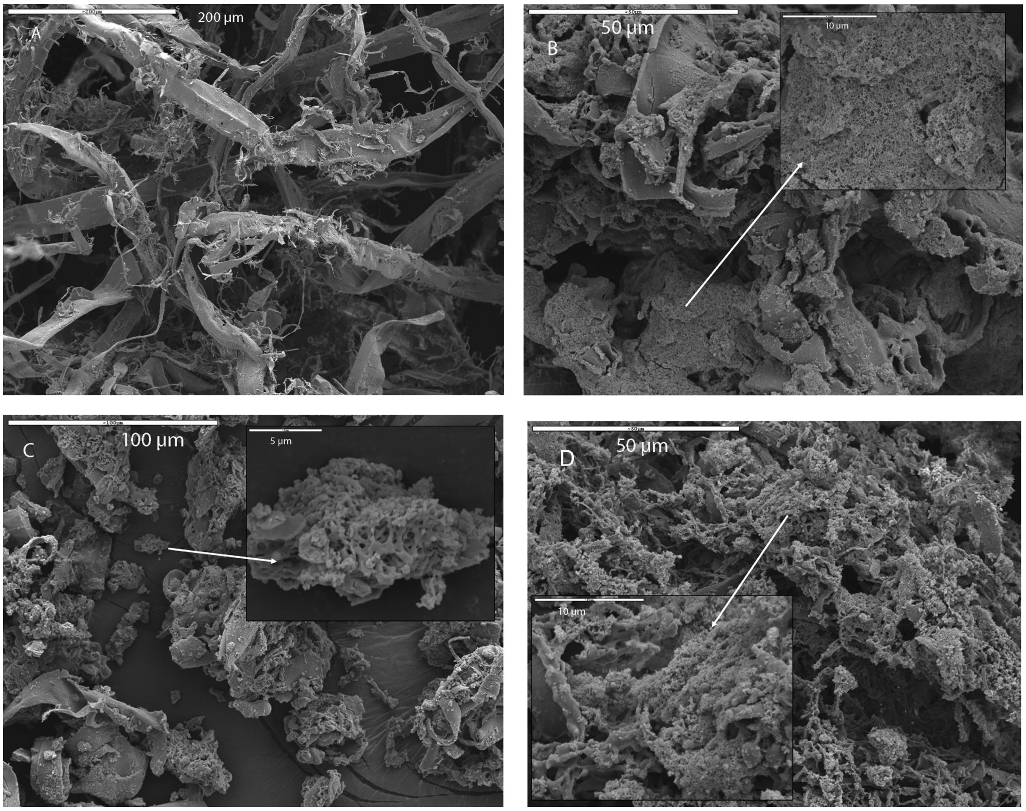


Figure 8. SEM photomicrographs of (A) spruce TMP; (B) acetylated spruce with 65% WPG (entry A7, Table 1) with a DS of 92.6%; (C) benzoylated spruce with 150% WPG (entry B2, Table 2) with a DS of 94.0%; (D) carbanilated spruce with 165% of WPG (entry C5, Table 3) with a DS of 89.7%.

provided by the bulkier phenyl groups present on the benzoylated derivative as opposed to the smaller acetate. The thermograms of the carbanilated wood, however, provided no significant information and as such are not shown.

3.7. Morphological Investigation of Wood and Wood Derivatives. To better understand and couple the thermal properties of the wood derivatives produced to product performance and other utilization characteristics, the morphology of the wood derivatives produced was also examined using scanning electron microscopy (SEM). Figure 8 shows the comparative microphotographs. The photomicrographs of the wood derivatives show a highly porous and considerably more uniform and isotropic structure throughout. Such morphological properties, when coupled with the chemical and thermal characteristics of the new materials, could offer significant benefits as far as increased compatibility and improved processability of wood with synthetic polymers are concerned.[24] Such avenues are currently being explored in our laboratory and will be the subject of future communications and patent disclosures.[25]

4. Conclusion

The homogenous effective acetylation, benzoylation, and carbanilation reactions on lignocellulosic materials have been carried out in ionic liquids. The use of quantitative ^{31}P NMR coupled with weight percent gain values was utilized to understand and optimize the reaction conditions. Highly substituted wood-based lignocellulosic derivatives have been obtained with high degrees of reproducibility. The resulting wood derivatives are materials that show distinct thermal transitions, high porosity, and uniform morphology. Overall, we envisage that the coupling of abundant lignocellulosic raw materials with environmentally benign ionic liquid solvents will offer significantly new technology platforms for wood and wood component utilization.

Supporting Information Available. ^{1}H NMR spectra of fresh and recycled ionic liquid [bmim]Cl; IR spectra of wood and wood derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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