Mild Synthesis of Benzylated Bamboo in LiCl/DMSO Solution

Ming-Fei Li,[1] Shao-Ni Sun,[1] Feng Xu,[1,2] Run-Cang Sun[1,3]

[1]*Institute of Biomass Chemistry and Technology, Beijing Forestry University, 100083 Beijing, China*
[2]*College of Light Chemistry and Textile Engineering, Qiqihar University, 161006 Qiqihar, China*
[3]*State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, 510640 Guangzhou, China*

ABSTRACT: Benzylated bamboo was mildly synthesized in nonaqueous medium without mercerization pretreatment. The ball-milled bamboo was firstly preswelled in lithium chloride/dimethyl sulfoxide (LiCl/DMSO) solution and then reacted with benzyl chloride in the presence of solid NaOH with varying molar ratios of benzyl chloride to OH groups of bamboo (1–4), reaction times (1–8 h), and temperatures (60–90°C). Benzylated bamboo products with yields from 51.1 to 106.9% and with degrees of substitution [DS, apparent value evaluated by Fourier transform infrared (FTIR) spectra] between 0.2 and 1.2 were synthesized. FTIR and ^{13}C cross polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectroscopy confirmed the incorporation of benzyl groups into bamboo; SEM observations of the highly benzylated bamboo showed porous surface with small irregular slices ascribed to the disruption of intermolecular and intramolecular hydrogen bonds between cellulose. Because of the degradation of amorphous components, the crystallinity decreased negligibly after modification and the thermal stability increased slightly but was lower than that of cellulose. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 274–282, 2012

Key words: benzylation; Fourier transform infrared; lithium chloride/dimethyl sulfoxide; nuclear magnetic resonance; thermal properties

INTRODUCTION

Currently, there are national initiatives for promoting the production and use of fuels, chemicals, and materials from lignocelluloses in response to the challenge of fossil fuel shortage.[1,2] Lignocelluloses represent abundant natural renewable resources that can be used to produce sustainable energy and materials. Generally, lignocelluloses are composed of three main components: cellulose, hemicelluloses, and lignin.[3,4] Cellulose is a linear polymer composed of D-glucose subunits linked by β-1,4 glycosidic bonds with crystalline and amorphous regions. The cellulose strains are bundled together to form cellulose fibrils, which are mostly independent and weakly bound through hydrogen bonding.[5] Hemicelluloses are complex heterogeneous polysaccharides that consist of different monosaccharides mainly including pentoses (xylose and arabinose), hexoses (mannose, glucose and galactose), and sugar acids.[6] Lignin is an amorphous heteropolymer consisting of three different phenylpropane units (p-coumaryl, coniferyl, and sinapyl alcohol) that are held together by different kinds of linkages.[7]

Lignocelluloses cannot be melted and melded directly, which is mainly due to the high crystallinity of cellulose (up to 50–70%).[8] Cellulose has the highest soften temperature among the lignocellulosic components, and its properties (strength, stiffness, and absorptive capacity) are due to its strong inter- and intrachain hydrogen bonds. This situation can change, however, if some groups in the lignocelluloses are substituted via modification. By chemical modification of lignocelluloses through substitution of hydroxyl groups in the cellulose molecule with nonpolar groups, novel properties can be introduced thus broaden their applications.[9] Especially importance was those modifications introducing substantially qualitative changes, such as thermal plasticity, which can improve the processability of lignocelluloses for the preparation of films, sheets,

molded products, etc. Generally, modifications of lignocellulosic material are achieved through esterification and etherification. Over the past years, a great deal of research has been conducted on making cellulose,[10–12] pulp,[13–16] wood,[17–19] and agro-fiber[20–22] into thermoplastics that are biodegradable and water resistant through benzylation. Benzylation of the hydroxyl groups in lignocelluloses can aid in bulking the lignocelluloses as well as disrupting the hydrogen bonding between adjacent chains and thus making the modified polymer thermoformable. Conventionally, lignocelluloses and cellulose were benzylated in aqueous NaOH solution at high concentrations (more than 20%).[15,17] The sample was mercerized with concentrated NaOH to break the crystalline structure before synthesis. However, under these conditions, hydrolysis of hemicelluloses and degradation of lignin can occur due to the alkaline medium at elevated temperatures of more than 150°C.[23] Therefore, the mercerization pretreatment step was conducted at room temperature and the subsequent benzylation step was around 110°C as usual. In the conventional benzylation process, some components, such as degraded carbohydrates and lignin, were lost in the washing step after mercerization. Furthermore, the hydrolysis reactions of cellulose, hemicelluloses, and lignin occurred due to the high amount of water in the reaction system.

Bamboo, an abundantly available grassy lignocellulose, if modified by benzyltion, can be used for the preparation of sheets, films, and molded products. Furthermore, wood plastic composites, such as cured plasticlike wooden boards, would be another potential use for benzyltated bamboo. Lithium chloride/dimethyl sulfoxide (LiCl/DMSO) solvent presented as a good system to dissolve regenerated cellulose firstly,[24] and applied to treat wood for components separation in recent years.[25–27] In contrast, etherification of lignocelluloses in this system is still an open question. As etherification of lignocelluloses starting by nonaqueous solvents can reduce the reagent loss by hydrolysis in the synthesis process, it was hoped that this solution would be a good system for benzylation. Therefore, the aim of the present study was to explore a novel method to prepare benzylated bamboo by using LiCl/DMSO solution in a direct way. In this case, LiCl/DMSO solution was used as a pretreatment agent as well as a reaction medium to prepare benzylated bamboo with varying degrees of substitution (DS). In addition, the benzylated bamboo products were characterized with Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. Furthermore, the thermal stability, crystallinity as well as morphology were investigated with respect to different DS.

TABLE I
Synthesis of Benzylated Bamboo Under Varying Conditions

Sample	Molar ratio	Temperature (°C)	Time (h)
S1	1	80	4
S2	2	80	4
S3	3	80	4
S4	4	80	4
S5	3	60	4
S6	3	70	4
S7	3	90	4
S8	3	70	1
S9	3	70	2
S10	3	70	8

EXPERIMENTAL

Materials

The dewaxed Bamboo (*Neosinocalamus affinis*) prepared according to a previous report,[28] was used in the present experiment. The composition was glucose 50.82%, xylose 22.94%, arabinose 1.13%, galactose 0.51%, mannose 0.37%, rhamnose 0.02%, glucuronic acid 0.94%, lignin 19.46% (Klason lignin 16.97% and acid-soluble lignin 2.49%), and ash 2.52%. The bamboo was milled with porcelain balls in a porcelain jar before use. All chemicals used in the experiment were analytical grade reagents, and were used without further purification. The amount of OH groups in the dewaxed bamboo was calculated referring to the method proposed by Rowell[29] according to the chemical composition of the raw material: $0.1946 \times 1.47/206.8 + (0.5082 + 0.0051 + 0.0037) \times 3/162 + (0.2294 + 0.0113 + 0.0002) \times 2/132 = 14.61 \times 10^{-3}$ mol/g. For this formula, 1.47 means the total OH groups per C_9 unit of lignin (determined by ^{1}H-NMR), and 206.8 means the molecular weight of the lignin $[C_9H_{8.40}O_{3.02}(OCH_3)_{1.35}]$ calculated by elemental analysis[30]; 3 means the OH groups per C_6 unit and 162 means the molecular weight of C6 type sugars; 2 means the OH groups per C_5 unit and 132 means the molecular weight of C5 type sugars.

Synthesis of benzylated bamboo

The benzylation reactions were conducted under varying molar ratios of benzyl chloride to OH groups of bamboo (1–4), reaction times (1–8 h), and reaction temperatures (60–90°C), as illustrated in Table I. In a typical preparation, for example (S6), 1 g of ball-milled bamboo was slurred in a mixture of 40 g LiCl/DMSO solution (6% LiCl dissolved in DMSO). After stirring for 2 h at room temperature to afford a lignocellulose gel, a suspension of 1.74 g (43.83 mmol) NaOH in 10 g DMSO was added followed by the addition of 5.10 mL (43.83 mmol) benzyl chloride (note: the mole of benzyl chloride was
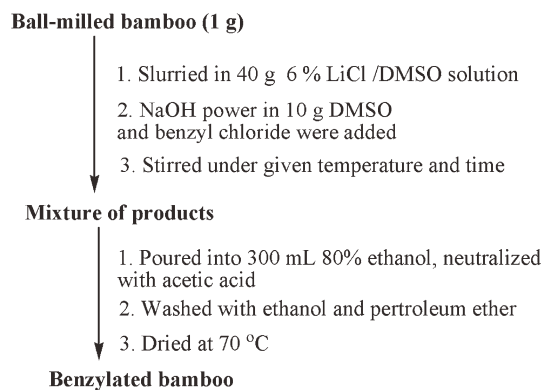
Ball-milled bamboo (1 g)

1. Slurried in 40 g 6 % LiCl /DMSO solution

2. NaOH power in 10 g DMSO
and benzyl chloride were added

3. Stirred under given temperature and time

Mixture of products

1. Poured into 300 mL 80% ethanol, neutralized
with acetic acid

2. Washed with ethanol and pertroleum ether

3. Dried at 70 °C

Benzylated bamboo

Figure 1 Scheme for benzylation of bamboo in LiCl/DMSO solution.

equal to that of solid NaOH). Then the temperature was raised to 70°C. After stirring for 4 h the mixture was cooled down to room temperature and poured into 300 mL 80% (v/v) aqueous ethanol. The mixture was neutralized with acetic acid and the product was filtered off, washed with 80% (v/v) aqueous ethanol, and then washed thoroughly with ethanol and petroleum ether and dried at 70°C. The scheme for benzylation is illustrated in Figure 1.

Characterization of the benzylated bamboo products

The apparent DS was defined in the resent study according to a previous study[17] by the formula: DS = A (736 cm^{-1})/A (2877 cm^{-1}), where A represents the absorption of the peak. FTIR spectra of the samples were obtained on a spectrophotometer (Bruker) using KBr disks containing 1% finely ground samples. For each sample, the data were recorded from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1} with an accumulation of 32 scans. CP/MAS ^{13}C-NMR spectra were recorded on a Bruker AV-III 400 M spectrometer (100 MHz) at 25°C with 4 mm MAS BBO probe. About 250 mg of sample was packed into zirconia rotors for MAS. The measurement was performed using a CP pulse program with acquisition time 0.034 s, delay time 2 s, and accumulation 5000 scans.

X-ray diffractograms of samples were obtained by using XRD-6000 instrument (Shimidzu, Japan). The preparations were laid on a glass sample holder and analyzed under plateau conditions. The X-ray diffractograms were recorded from 5 to 40° (2θ) at a

scanning speed of 5°/min. To determine the crystallinity index (CrI), the total diffracted area and the area under the crystalline peaks were determined by integration after correcting the data for absorption, and the ratio of the crystalline area to that of the total diffracted area was taken as CrI.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the samples were investigated by a simultaneous thermal analyzer (DTG-60, Shimadzu, Japan). Samples weighed 8–10 mg were heated in an aluminum crucible from room temperature to 600°C at a heating rate of 10°C/min. The apparatus was continually flushed with nitrogen at a flow rate of 30 mL/min.

For morphological observation, the air-dried samples were coated with gold–palladium in a sputter coater (E-1010, HITACHI, Japan). Then scanning electron micrographs (SEM) were observed with a scanning electron microscope (S-3400N, HITACHI, Japan) at acceleration voltages of 10 kV.

RESULTS AND DISCUSSION

Effects of reaction parameters on benzylation

In this study, the ball-milled bamboo was pre-swelled with LiCl/DMSO before synthesis. Under this condition, undissociated ion pairs of LiCl molecules in a polar aprotic solvent (DMSO) might interact with the oxygen atoms of hydroxyl groups, and thus, disrupted and prevented reformation of hydrogen bonds between cellulose molecules,[25] whereby breaking the rigid structure to facilitate the subsequent synthesis. Benzylation of bamboo in LiCl/DMSO solution is a typical Williamson synthesis reaction involving nucleophilic substitution of alkoxide for halide ion as shown in the scheme (Fig. 2).[31–33] It is difficult to calculate the DS, which is commonly used as an index of substitution for cellulose. Theoretically, the weights of lignocelluloses increase after benzylation, which has been confirmed by previous studies on wood,[17] ramie fiber,[21] and sisal fiber[34] in concentrated NaOH solutions under the given conditions. Generally, percentage of weight gain of the benzylated product could be used to evaluate the degree of benzylation. However, the weight of the product was resulted from both benzyl incorporation and components elimination of the original material.[34] Hence, the apparent DS of bamboo was used to evaluate the extent of the
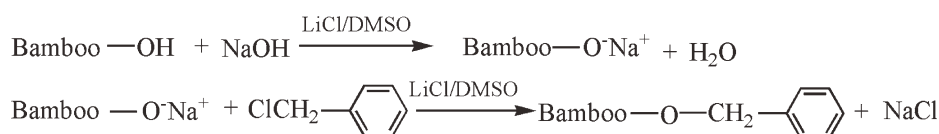
Bamboo —OH + NaOH $\xrightarrow{\text{LiCl/DMSO}}$ Bamboo—O⁻Na⁺ + H₂O

Bamboo — O⁻Na⁺ + ClCH₂—⟨⟩ $\xrightarrow{\text{LiCl/DMSO}}$ Bamboo—O—CH₂—⟨⟩ + NaCl

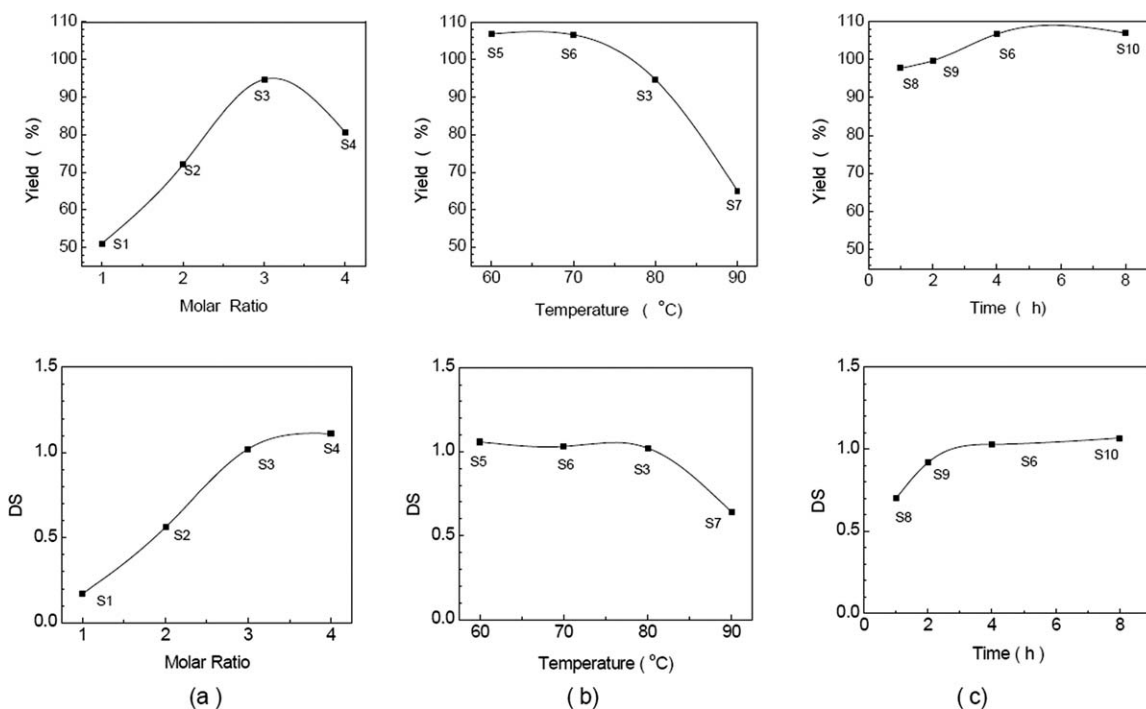**Figure 2** Main reactions of bamboo in benzylation.

Figure 3 Effects of reaction conditions on the yield and DS of benzylated bamboo: (a) molar ratio; (b) reaction temperature; (c) reaction time.

incorporation of the benzyl groups as indicated in the Experimental part.

During the synthesis process, several factors influenced the degree of benzylation. These factors included the molar ratio of benzyl chloride to OH groups in lignocellulose, reaction temperature, and time. An optimization of benzylation process of bamboo was investigated by varying a certain reaction parameter while other parameters were kept constant. To evaluate the benzyl groups in benzyl chloride on the benzyltion reaction, an equal molar of NaOH was added in the reaction system to eliminate the effect of the produced HCl during the reaction process. The effects of molar ratios of benzyl groups to bamboo (1–4), reaction times (1–8 h), and reaction temperatures (60–90°C) on the DS and yield of the benzylated bamboo were investigated in this study, and the results were summarized in Figure 3. As can be seen from Figure 3(a), when temperature retained 80°C and the duration was 4 h, increase of molar ratio from 1 to 3 resulted in a sharp increase of DS of benzylated products from 0.17 to 1.02, accompanying an increase of yield from 51.1 to 94.8%. However, when molar ratio increased from 3 to 4, there was a slight increase of DS from 1.02 to 1.11 while the product yield decreased from 94.8 to 80.7%. This suggested that low amounts of benzylation agents led to degradation and dissolution of extractable components, and improving the amounts of benzylation agents can increase the probability of molecular collision resulting in higher incorporation

of benzyl groups. In the presence of higher amounts of benzyl chloride, the decrease of product yield might be due to the preferential degradation reaction of lignocelluloses. Generally, two types of reactions, incorporation of benzyl groups into lignocelluloses and degradation reaction of lignocelluloses to produce low molecular weight substances, occurred simultaneously during the synthesis process.

When the molar ratio was 3 and the duration was 4 h, with the increase of temperature from 60 to 70°C, there was a slight decrease of DS from 1.06 to 1.03, accompanying a negligible decrease of yield of the product [Fig. 3(b)]. However, with a further increase of temperature from 70 to 90°C, there was a sharp decrease of DS from 1.03 to 0.64. This suggested that there was no significant influence of temperature on the synthesis reaction at lower temperature, whereas a higher temperature would result in decreases of both DS and yield. This phenomenon was different from the benzylation of wood in aqueous NaOH, in which increase of temperature from 60 to 110°C resulted in a significant increase of DS.[17] Obviously, the results in the present study indicated that benzylation of lignocellulose in LiCl/DMSO system preferentially occurred at a relatively low temperature as compared to in aqueous NaOH.

The effects of reaction time on the product yield and DS of the benzylated lignocelluloses were estimated at 70°C with molar ratio of 3 [Fig. 3(c)]. Extending the reaction time from 1 to 2, 4, and 8 h resulted in the improvement of DS from 0.70 to 0.92,
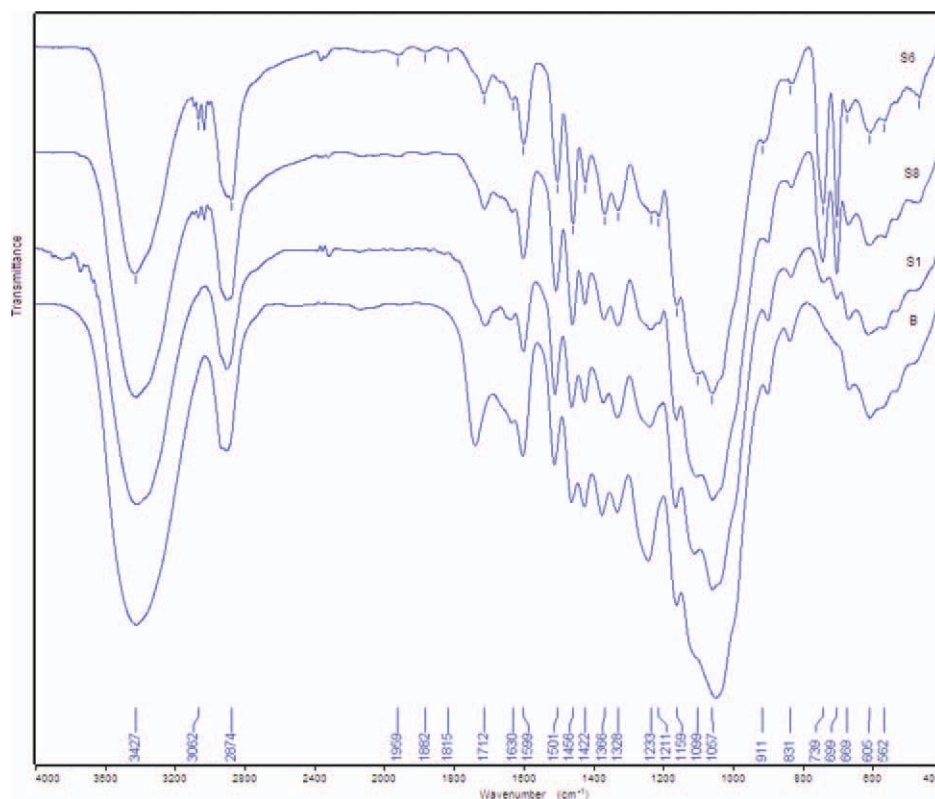
Figure 4 FTIR spectra of benzylated bamboo with varying DS (S6, S8, and S1) as compared to the native bamboo (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1.03, and 1.07, and an increase of the product yield from 97.8 to 99.7, 106.7, and 106.9%, respectively. This indicated that the degradation rate was greater than the benzylation rate in the initial stage. After 4 h, a high benzylation rate resulted in the increase of yield over 100%.

From the above analysis, it was suggested that the optimal reaction conditions for benzylation of bamboo were molar ratio 3, reaction temperature 70°C, and reaction time 4 h, which produced the benzylated bamboo with a yield of 106.7% and a DS of 1.03. This preferential mild reaction condition indicated that the benzylation of lignocellulose could be achieved in nonaqueous solution at a lower temperature, as compared to that at aqueous NaOH.[19]

FTIR spectra analysis

The FTIR spectra shown in Figure 4, corresponding to the substituted bamboo with higher (S8 and S6) and lower (S1) DS as compared to the native bamboo (B), demonstrated the remarkable changes of the structure caused by the introduction of benzyl groups to the bamboo. Obviously, the FTIR profiles of benzylated samples are extremely similar to those of benzylated wood[19] and agro-fiber[21] prepared in aqueous NaOH solution. Hydroxyl vibration absorption at 3400 cm^{-1} is significantly diminished after

benzylation due to the etherification of hydroxyl groups. Further evidence of benzylation of bamboo can be examined by the occurrence and intensity of the bands arising from the appearance of aromatic moieties at 3087–3004 cm^{-1} (corresponding to aromatic C—H deformation), 739 cm^{-1} (aromatic C—H angular out-of-plane deformation), and 699 cm^{-1} (aromatic C—H angular deformation) increased due to aromatic rings, indicating that hydroxyl groups were substituted by aromatic groups.[35] The intensity of aryl rings absorption at 1599, 1501, and 1460 cm^{-1} increased with the increase of substitution. The triplet-peaks at 1957, 1879, and 1815 cm^{-1} (appeared in the benzylated bamboo with a higher DS) and the doublet-peaks at 739 and 699 cm^{-1} strongly displayed the characteristic of mono-substituted benzene rings of benzyl groups, which were also found in benzylated sugar cane bagasse in a previous study.[13] In addition, the increase of the ratio of the peak height at 739 cm^{-1} (benzyl groups) to that at 2877 cm^{-1} (methane or methyl components), as well as the decrease of ratio of the height at 3419 cm^{-1} (hydroxyl groups) to that at 2877 cm^{-1} confirmed that the substitution of hydroxyl groups in bamboo with benzyl groups occurred. Furthermore, the band at 1730 cm^{-1} is attributed to acetyl and carboxyl groups of hemicelluloses and aliphatic ketone or aldehyde groups in lignin structure.[36] This
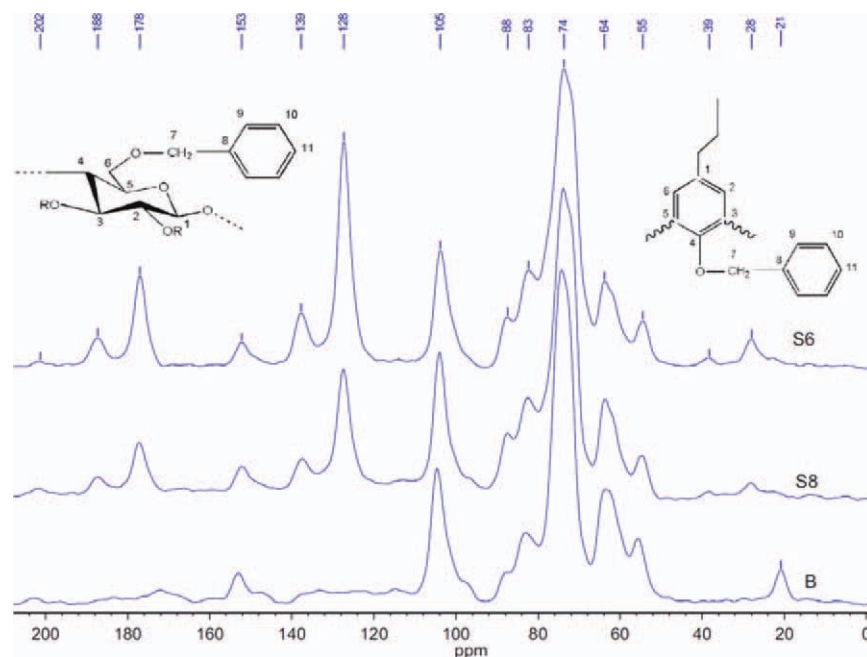
Figure 5 CP MAS ^{13}C-NMR spectra of benzylated bamboo with varying DS (S6 and S8) as compared to the native bamboo (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorption band is significantly reduced after benzylation due to the alkaline medium. These results of IR strongly indicated that bamboo was successfully benzylated under the conditions in this study.

CP/MAS NMR spectra analysis

Solid state CP/MAS ^{13}C-NMR spectra of the benzylated products (S6 and S8) as compared to the native bamboo (B) were used to investigate chemical information on benzylation (Fig. 5). The spectrum of bamboo shows prominent signals between 60 and 110 ppm associated with carbohydrates (cellulose and hemicelluloses). Cellulose shows signals at 60–70 ppm (C6), 70–80 ppm (C2, C3, and C5), 80–90 ppm (C4), and 98–110 ppm (C1). In addition, xylan exhibits signals at 103 ppm (C1), 84 ppm (C4), 72–75 ppm (C2 and C3), and 65 ppm (C5), which overlap with the signals of cellulose.[37] The signals at 88 and 83 ppm are assigned to the crystalline and amorphous regions of C4. In addition, the signals at 68 and 65 ppm are assigned to crystalline and amorphous regions of C6 in cellulose. Moreover, resonances at 174 and 21 ppm are originated from the acetyl groups. The less intense signals at 58, 115–130, and 152–156 ppm, are associated with methoxyl and aromatic groups of lignin.

In the benzylated bamboo samples, an intense signal appeared at 128 ppm corresponds to C9, C10, and C11 of benzyl groups substituted to position C6 of cellulose. The signal at 139 ppm is assigned to C4 on benzylated *p*-hydroxyl phenyl, guaiacyl, and syringl units.[19] Obviously, the above signals increase

with the increase of DS. In addition, the sharp signal at 178 ppm is due to carbonyl groups.

Crystal structure

Crystal structure of benzylated bamboo was investigated with X-ray diffractometer. The recorded X-ray diffraction patterns of the benzylated bamboo with different DS (S6, S8, and S1) are shown in Figure 6 as compared to the native bamboo (B) and regenerated bamboo (RB). The native bamboo sample presented an X-ray pattern characteristic of cellulose I type of material, with a main diffraction peak at 2θ = 21.9° associated with the diffraction of 002 plane. Another minor peak at 2θ = 16.3° can be observed due to the diffraction of planes 101 and 10$\bar{1}$.[38] After the sample was regenerated from LiCl/DMSO solution, there was a slight increase of the intensity of the peak around 16.3°. Compared to the RB, the intensity of the peak around 16.3° in the benzylated bamboo decreased and slightly shifted to 16.1° and the peak at 21.9° moved to 21.0°.

In addition, the crystallinity of the bamboo decreased negligibly after modification. The calculated CrI of the benzylated bamboo samples ranged from 38.7 to 39.7%, as compared to 39.3% for bamboo and 40.9% for the RB. These results indicated that the preswelling and modification of bamboo in LiCl/DMSO solution did not disrupt the crystallinity structure of bamboo significantly. These results were obviously different from the conventional ways of benzylation of lignocelluloses[34,39] and cellulose[15] in concentrated aqueous NaOH applying mercerization
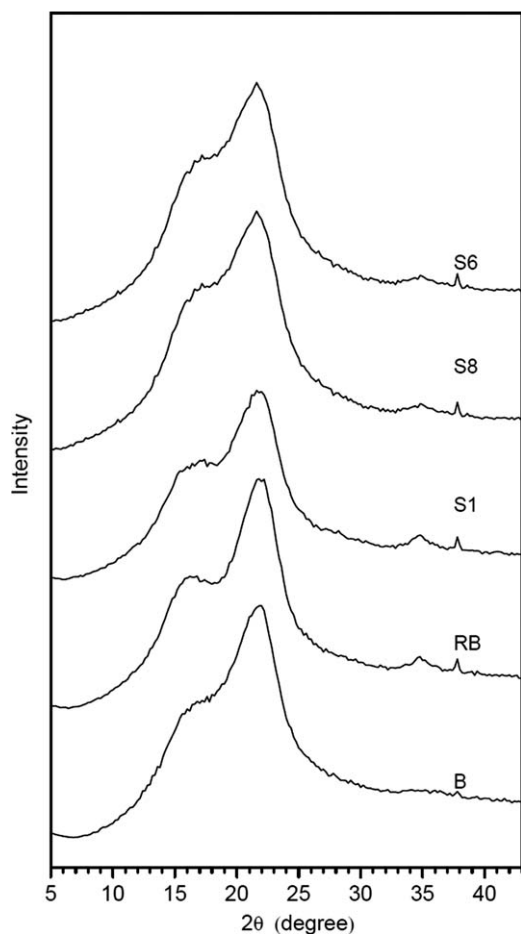
Figure 6 X-ray diffraction patterns of benzylated bamboo with varying DS (S6, S8, and S1) as compared to the RB and the native bamboo (B).

pretreatment, in which change of cellulose I to cellulose II happened and a significant decrystallization occurred. The nonsignificant changes of the crystallinity might be due to the relative weak breaking force of the LiCl/DMSO solution as compared to the concentrated alkaline solution. In fact, benzylation led to decrease of the crystallinity of cellulose due to the incorporation of benzyl groups. However, under such conditions, degradation of some amorphous components such as carbohydrates and lignin resulted in decrease of proportion of amorphous components, as indicated by the low yield of the products, thus exhibited the negligible changes of CrI.

Thermal properties

The effect of benzylation on the thermal properties of bamboo was also investigated by TGA and DTA in the temperature range from room temperature to 600°C under nitrogen atmosphere. TG, DTG, and DTA curves of the benzylated bamboo as compared to the native bamboo are illustrated in Figure 7. As can be seen from Figure 7(a,b), in the initial stage,

the slight decrease of weight from 60 to 110°C was associated with absorbed water in the samples. The absorbed water decreased approximately from 2.0% for native samples to around 0.1% for the benzylated samples. After that, bamboo began to degrade at 194°C mainly due to hemicelluloses, and subsequently at 310°C mainly associated with cellulose, whereas the benzylated samples S8 (DS 0.70) and S6 (DS 1.03) began to degrade at 261 and 262°C, respectively. This suggested that the thermal stability of the benzylated lignocellulose was slightly higher than that of the native bamboo sample, but lower than of the cellulose component. Increase of thermal stability of lignocelluloses was also observed in the initial stage of benzylation of sisal fibers.[34] Actually, decrease of thermal stability was widely reported after benzylation of cellulose.[11,15] The maximum decomposition rate was 8.4%/min at 347°C for bamboo, whereas 10.1%/min at 343°C for S8, and 10.4%/min at 341°C for S6. The decrease of the temperature at the maximum degradation rate was due to the chain fragmentation of the lignocellulosic components during the reaction.[39] When temperature was up to 600°C, 16.7% and 13.7% of the initial weight remained for S8 and S6, as compared to a relatively high value of 22.5% for bamboo.

With the aim of identifying the heat flow of the samples, DTA curves were recorded [Fig. 7(c)]. An
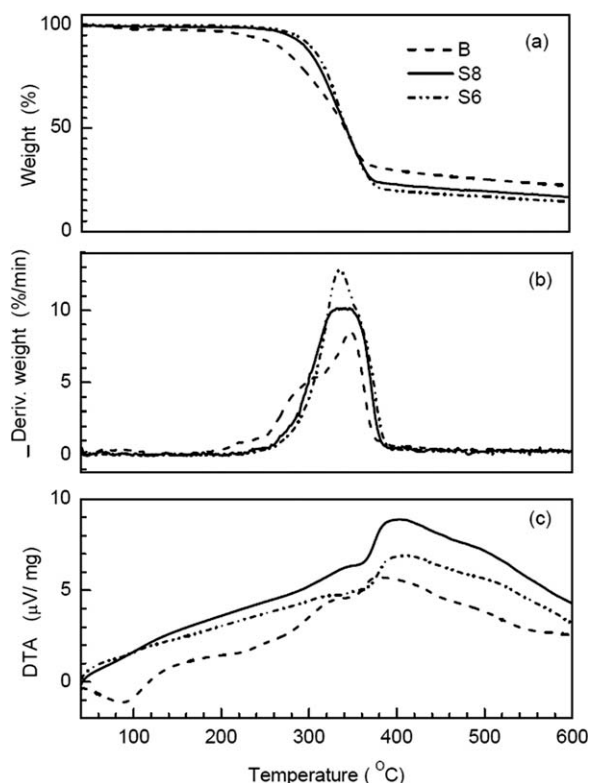

Figure 7 TG, DTG, and DTA curves of benzylated bamboo with varying DS (S6 and S8) as compared to the native bamboo (B).
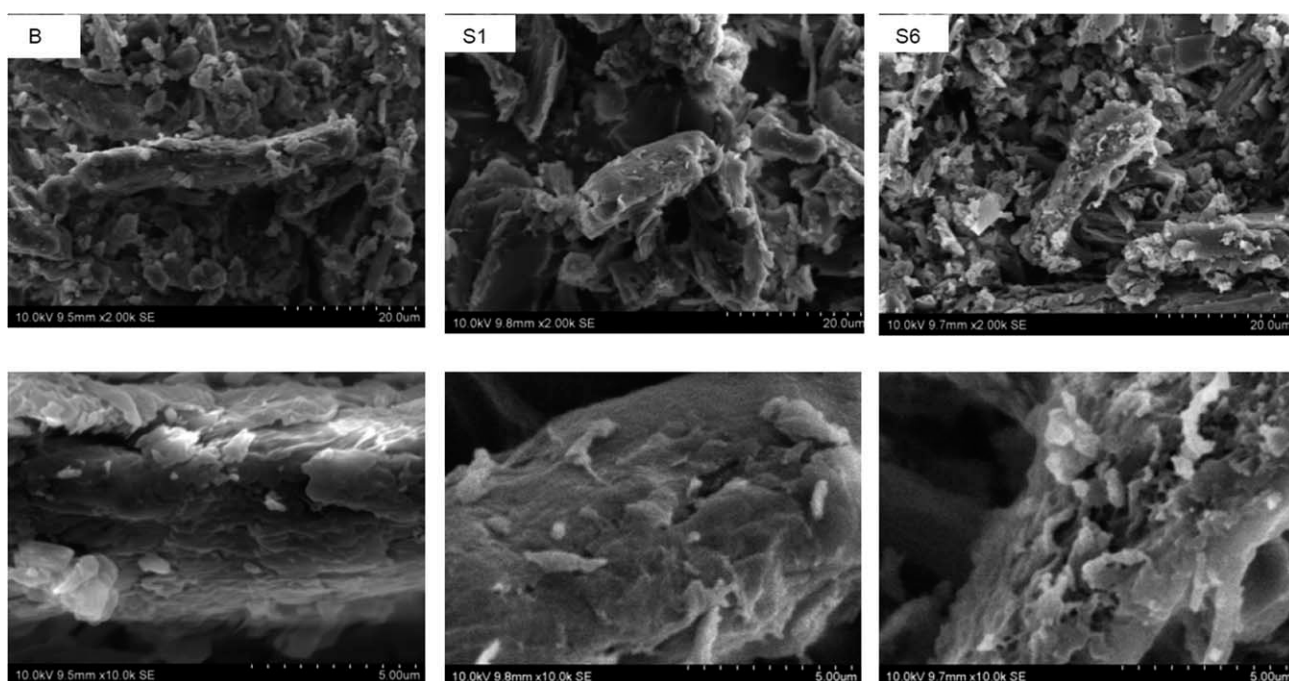
Figure 8 SEM images of benzylated bamboo with varying DS (S6 and S1) as compared to the native bamboo (B).

endothermic peak is observed around 100°C for the native bamboo. However, this endothermic peak disappeared in the benzylated bamboo samples (S8 and S6), which was in agreement with their low moisture absorption.[20] In the temperature range from 300 to 500°C, the maximum exothermic peaks are observed at around 398°C for the two benzylated samples, as compared to a low temperature at 372°C for the native bamboo. The shift of the peak to higher temperature after benzylation was in well agreement with the slight increase of the thermal stability.

Surface morphology

Scanning electron microscopy (SEM) was performed on the benzylated bamboo as well as on the native sample to examine the changes of surface morphology (Fig. 8). The native ball-milled bamboo (B) showed rigid shape, and after benzylation, the surface changed. Benzylated sample with low substitution (S1) still showed rigid structure though the surface crack of ball-milled bamboo could be distinguished, whereas the sample with a higher substitution (S6) did not exhibit rigid surface of particle but showed porous surface and small irregular slices, and the surface became rather coarse and rough. The above observations indicated that with the increase of degree of benzylation, the incorporation of more benzyl groups resulted in the increasing disruption of intermolecular and intramolecular hydrogen bonds, thus destroyed the rigid structure of bamboo particle. Similar phenomenon has also been investigated by other researchers about benzylation of wood. It was reported that rigid fibers presented in a less benzylated wood sample, whereas no fibers were observed in benzylated wood with a high substitution.[18,19]

CONCLUSIONS

Based on the results above, the following conclusions were drawn: (1) benzylated bamboo can be synthesized in LiCl/DMSO solution without mercerization via concentrated NaOH solution. The preferential mild reaction conditions suggested that benzylation of lignocellulose could be achieved in nonaqueous solution at a relatively low temperature. The suggested optimal reaction conditions for benzylation of bamboo were molar ratio of benzyl chloride to OH groups in bamboo 3, reaction temperature 70°C, and reaction time 4 h, which produced benzylated bamboo with a yield of 106.7% and a DS of 1.03. (2) FTIR and CP/MAS NMR spectroscopy confirmed the incorporation of benzyl groups into bamboo; SEM observations of the highly benzylated bamboo showed porous surface with small irregular slices ascribed to the disruption of intermolecular and intramolecular hydrogen bonds. (3) The crystallinity of bamboo decreased negligibly after modification due to the degradation of amorphous components, and the thermal stability slightly increased but was lower than that of cellulose.

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