

## BENZYLATION AND CHARACTERIZATION OF COLD NaOH/UREA PRE-SWELLED BAMBOO

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Ball-milled bamboo was pre-swelled with a cold aqueous solution of NaOH and urea, and then reacted directly with benzyl chloride to synthesize benzylated bamboo. The effects of the molar ratio of benzyl chloride to OH groups in the bamboo (1 to 4), the reaction temperature (70 to 110 °C), and the reaction time (2 to 8 h) on both the product yield and the degree of substitution (DS) were evaluated. Yields between 67.6 and 94.0% and DS between 0.31 and 0.74 of the benzylated bamboo were obtained under such conditions. The incorporation of benzyl groups was evidenced by FT-IR and CP/MAS <sup>13</sup>C-NMR spectroscopy. It was found that the crystalline structure of the native ball-milled bamboo was markedly damaged after modification. In addition, the benzylated bamboo was subjected to thermal degradation at a high temperature with an increase in substitution. It was suggested that the benzylated bamboo with a low crystallinity as well as large non-polar groups is promising as a filler for use in the composite material industry.

*Keywords:* Benzylation; Etherification; NaOH/urea aqueous solution; NMR; Thermal stability

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### INTRODUCTION

With the increasing demand for biodegradable polymers from natural resources, much effort has been devoted to exploring lignocelluloses for several end uses. Lignocelluloses principally consist of cellulose, hemicelluloses, and lignin (Yarbrough et al. 2009; Dick-Pérez et al. 2011). Cellulose is the main structural component in lignocelluloses and consists entirely of non-branched  $\beta$ -1,4-linked glucose with crystalline and amorphous regions. Hemicelluloses are a heterogeneous class of polymers that contain pentoses (xylose and arabinose), hexoses (mannose, glucose, and galactose), and/or uronic acids (glucuronic, 4-*O*-methylgalacturonic, and galacturonic acids) linked by various glycoside bonds. Lignins are polymers that can incorporate different proportions of three types of phenylpropane units: *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S). Due to the high degree of crystallinity of cellulose as well as the three-dimensional net structure of lignin, lignocelluloses cannot be processed like thermoplastic polymers. Through certain substitution reactions on the side chains of cellulose in association with partial removal of lignin, however, many properties of lignocelluloses can be improved for further application in the material industry. The most abundant sites for reactivity on these polymers are the hydroxyl groups, and most reaction schemes have been based on the reactions of them.

Among the many approaches to chemical modification of lignocellulosic polymers, esterification or etherification are the most popular. In order of stability, the ether bond, as compared to the ester bond, is a more desirable covalent carbon-oxygen bond that can be formed in the reaction product. With respect to modification by etherification, benzylation has attracted much attention in recent years. Benzylation reactions occur between benzyl chloride and the hydroxyl groups of lignocelluloses, forming ether linkages attached to benzene rings, which makes lignocelluloses more compatible with non-polar matrices. Benzylation of lignocelluloses such as wood (Mohammadi-Rovshandeh 2003; Dominkovics et al. 2007), sisal fiber (Ferreira et al. 2003), bamboo fiber (Kushwaha and Kumar 2011), ramie fiber (Liu et al. 2008), oil palm empty fruit bunch (Zakaria et al. 2001), and olive residue (Djidjelli et al. 2008), has been successfully performed. It was reported that the benzylated lignocellulosic product is a good resource for the preparation of composites as compared to the native lignocelluloses, which had poor interfacial interaction with hydrophobic polymer matrices and hence decreased the mechanical properties of the composites (Zhang et al. 2005). The benzylated lignocellulose plastic composites showed low water absorption capacity, promising biodegradability, and acceptable mechanical properties (Lu et al. 2003; Zhang et al. 2005). In addition, a better dye efficiency was obtained when benzylated ramie fiber was dyed with disperse dyes (Liu et al. 2008); however, the reported reactions on benzylated lignocelluloses were mainly carried out via a conventional approach, i.e., synthesis at a high base concentration (40% NaOH) and temperature (110 °C) after mercerization pretreatment. It was reported that cellulose benzylation can be performed in novel solvents. For instance, the novel cellulose solvent DMSO/TBAF has been studied as a reaction medium for the synthesis of benzyl cellulose by treating the dissolved cellulose in the presence of solid NaOH under mild conditions (Ramos et al. 2005; Rohleder and Heinze 2010). Thus, searching for a novel modification approach on lignocellulose is a worthwhile effort.

Cold alkali/urea or thiourea solutions have attracted much attention in the dissolution of cellulose and pretreatment of lignocelluloses. It has been reported that NaOH/urea, NaOH/thiourea, and LiOH /urea aqueous systems (Cai and Zhang 2005, 2006; Cai et al. 2007; Cai et al. 2008), which are pre-cooled between -12 and -5 °C, can dissolve cellulose in a short time. The cellulose dissolution at a low temperature arises as a result of a fast dynamic self-assembly process among small molecules (NaOH, urea/thiourea and water) and cellulose macromolecules. The advantages of these solvent systems are lower costs and lower toxicity for the environment in comparison to other solvents such as NMMO/H<sub>2</sub>O, LiCl/DMAc, and ionic liquids (ILs) (Jin et al. 2007). The applications of these solvents at a low temperature are considered to be environmentally friendly processes because of the avoidance of evaporation of chemical agents. Novel cellulose fibers, membranes, microspheres, hydrogels, as well as cellulose derivatives for different potential applications have been successfully prepared (Luo and Zhang 2010) by using this dissolution method. Cellulose ethers, such as methylcellulose (Zhou et al. 2004), hydroxyethyl cellulose (Zhou et al. 2006), hydroxypropyl cellulose (Zhou et al. 2004), as well as cyanoethyl cellulose (Zhou et al. 2010) have been homogeneously synthesized in NaOH/urea aqueous systems under mild conditions without the addition of a catalyst due to the basicity of the solution. With respect to lignocelluloses, though, the

complete dissolution has not been reported presently, probably due to the complex structure of lignocelluloses; however, the NaOH/urea aqueous solution has been applied to pretreat lignocelluloses for bio-energy production and components separation due to the breaking force. After pretreatment with NaOH/urea aqueous solution at a low temperature, the enzymatic hydrolysis performance of spruce has been reported of being enhanced significantly (Zhao et al. 2008). In addition, the previous laboratory work conducted testified that the system can be used to treat bamboo for the separation of major components (Li et al. 2010, 2011); however, applying the system as a medium for lignocellulose synthesis is still an open question. Since NaOH/urea aqueous solution is alkaline, it may be a suitable reaction medium for the benzylation of lignocelluloses.

Bamboo, a perennial non-woody lignocellulose widely distributed in many Asian countries, is a promising feedstock for utilization due to its fast growth, short renovation cycle, and easy propagation (Scurlock et al. 2000). In the present study, therefore, NaOH/urea aqueous solution was studied as a pretreatment agent as well as a reaction medium for synthesis of benzylated bamboo. The benzylated bamboo products obtained were characterized by means of FT-IR, NMR, and XRD as well as thermal analysis. In addition, surface morphology changes of the substituted bamboo were also investigated.

## EXPERIMENTAL

### Materials

Dewaxed bamboo (*Neosinocalamus affinis*) was used in the present experiment. The composition was 50.82% glucose, 22.94% xylose, 1.13% arabinose, 0.51% galactose, 0.37% mannose, 0.02% rhamnose, 0.94% glucuronic acid, 19.46% lignin (Klason lignin 16.97% and acid-soluble lignin 2.49%), and 2.52% ash. The bamboo sample was milled with balls in accordance with a previous report before use (Li et al. 2010). All other chemicals of analytical grade were obtained from Beijing Chemical Regent Company, China, and used without further purification.

### Pre-swelling of Bamboo in Cold NaOH/urea Solution

The dried bamboo weighed 1 g (with 14.61 mmol OH groups, calculated in reference to the method proposed by Rowell (1980)) and was added to 49 g of 7% NaOH/12% urea aqueous solution and stirred for 5 min to obtain a slurry. After that, the slurry was frozen and then thawed with vigorous stirring for further use.

### Preparation of Benzylated Bamboo

The benzylation reactions were conducted under various molar ratios of benzyl chloride to OH groups (ratios between 1 and 4), reaction times (between 2 and 8 h), and reaction temperatures (between 70 and 110 °C), as illustrated in Table 1. In a typical preparation, for example (S2), 3.40 mL (29.22 mmol) of benzyl chloride was added to the slurry at room temperature. Subsequently, the slurry was transferred into a 100 mL round bottom flask. The reaction was conducted at 80 °C for 4 h with continuous stirring. Then the mixture was cooled to room temperature and poured into 300 mL of 80% (v/v) aqueous ethanol, followed by neutralization with acetic acid. The curded benzylated

bamboo products were collected by filtration, washed alternatively with 80% (v/v) aqueous ethanol and water, washed thoroughly with ethanol and petroleum ether, and finally dried at 70 °C. The yields of benzylated bamboo were determined gravimetrically.

**Table 1.** Conditions of Benzylation of Bamboo in NaOH/urea Aqueous Solution

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	70	4
S6	3	90	4
S7	3	110	4
S8	3	80	2
S9	3	80	6
S10	3	80	8

### Characterization of Benzylated Bamboo

FT-IR spectra were recorded with a spectrophotometer (Bruker) via pressing with KBr to pellets. For each sample, the data were collected from 4000 to 400  $\text{cm}^{-1}$  at a resolution of 2  $\text{cm}^{-1}$  with an accumulation of 32 scans. The apparent degree of substitution (DS) was defined in the present study according to a previous study by the formula:  $\text{DS} = A(740 \text{ cm}^{-1}) / A(2902 \text{ cm}^{-1})$ , where  $A$  represents the absorption of the peak, the peak at 740  $\text{cm}^{-1}$  is ascribed to aromatic C–H out-of-plane deformation from benzyl group, and the peak at 2902  $\text{cm}^{-1}$  is due to C–H stretching from methene and methyl groups from bamboo (Hon and Ou 1989). CP/MAS  $^{13}\text{C}$ -NMR spectra were acquired using a Bruker AV-III 400 M spectrometer (100 MHz) at 25 °C with a 4 mm MAS BBO probe. About 250 mg of the sample was packed into zirconia rotors for MAS. The measurement was performed using a CP pulse program with an acquisition time of 0.034 s, a delay time of 2 s, and an accumulation of 5000 scans.

X-ray diffractograms were obtained using an XRD-6000 instrument (Shimadzu, Japan). The preparations were laid on a glass sample holder and analyzed under plateau conditions. The X-ray diffractograms were recorded from 5° to 43° (2 $\theta$ ) 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 the CrI.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the samples were carried out on a simultaneous thermal analyzer (DTG-60, Shimadzu, Japan). Samples weighing between 8 and 10 mg were heated in an aluminum crucible

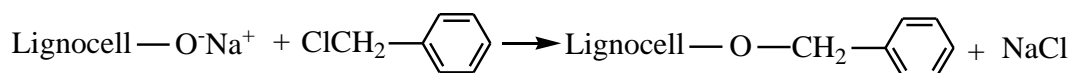
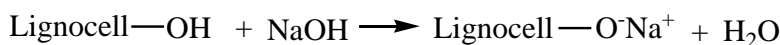
from room temperature to 600 °C at a heating rate of 10 °C/min. The apparatus was continually flushed with nitrogen at a flow rate of 30 mL/min.

Surface morphology analysis was examined with a scanning electron microscope (S-3400N, HITACHI, Japan) at acceleration voltages of 10 kV. All specimens were coated with gold-palladium in a sputter coater (E-1010, HITACHI, Japan) before observation.

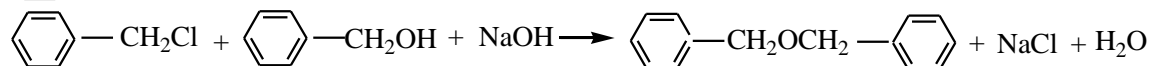
## RESULTS AND DISCUSSION

### Effect of the Reaction Parameters on Benzylation

Benylation of lignocellulose is a typical Williamson synthesis reaction involving nucleophilic substitution of an alkoxide or a phenoxide ion for a halide ion and is shown in the following reactions (Hon and Ou 1989; Zhang et al. 2005):



The side reactions include the following:

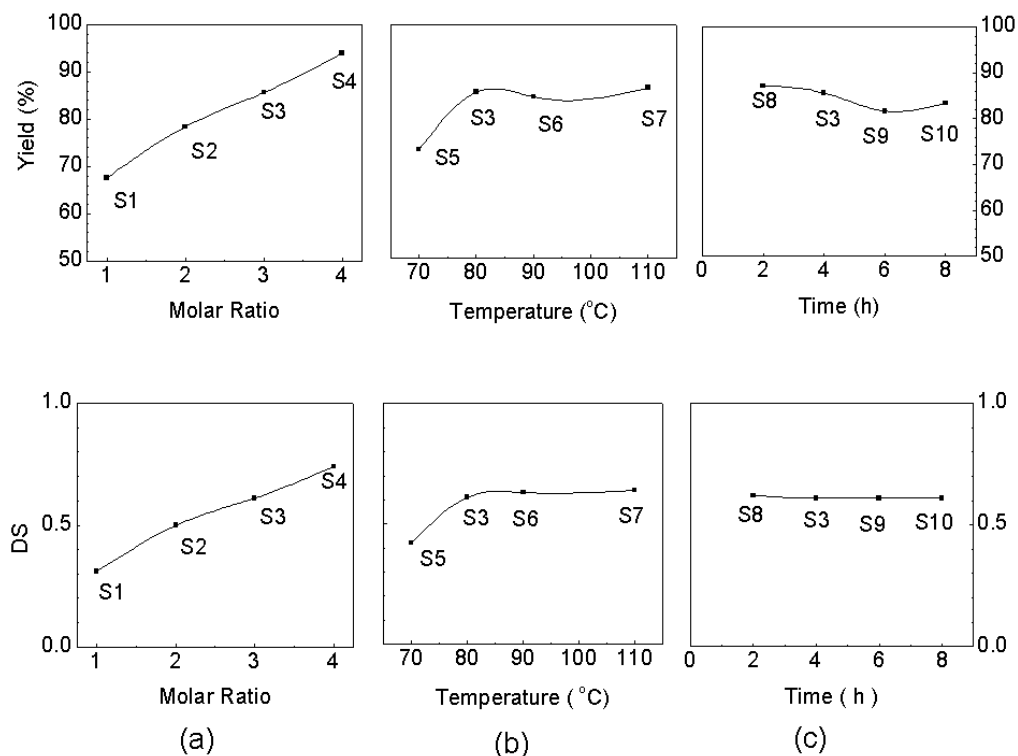


In addition, in alkaline solution, the major components of bamboo are partially degraded and dissolved in the solution. Cellulose and hemicelluloses are mainly hydrolyzed to form monosaccharides, oligosaccharides, etc.; whereas lignin is degraded into low molecular mass fragments. During the benzylation modification of bamboo starting from 7% NaOH/12% urea aqueous solution, several factors influenced the degree of substitution. These factors principally included the molar ratio of benzyl chloride to OH groups in bamboo, the reaction temperature, and the reaction time, according to a preliminary experiment. Thus, the optimization of the benzylation process was performed by varying the parameters above. Benzylation parameters were investigated by varying a single parameter while other parameters remained fixed. After an optimal parameter was obtained, the parameter value was used in the subsequent optimization step. The results obtained are illustrated in Fig. 1.

As shown in Fig. 1a, when the reactions were conducted at 80°C for 4 h, an increase in molar ratio from 1 to 2, 3, and 4 resulted in a steady increase in yield from 67.6 to 78.4, 85.6, and 94.0%, as well as an increase in DS from 0.31 to 0.50, 0.61, and 0.74, respectively. This suggested that an increase in the amount of benzyl chloride significantly increased both yield and DS, which was probably due to the greater availability of the benzyl chloride in the proximity of OH groups in bamboo at a higher concentration.

The effect of temperature on the yield and DS of benzylated product was estimated with a reaction time of 4 h and molar ratio of 3. As can be seen from Fig. 1b, as the temperature increased from 70 to 80 °C, the yield increased from 73.3 to 85.6%, and DS increased from 0.42 to 0.61. When the temperature was further increased from 80 to 90 and 110 °C, the yield varied from 85.6 to 84.5 and 86.5%, and DS slightly increased from 0.61 to 0.63 and 0.64, respectively. This was presumed to be due to the favorable effect of temperature on the etherification reaction. A higher temperature enhanced the mobility of the molecules, thus improving the probability of collisions between OH groups and benzyl chloride, resulting in an increase in the extent of benzylation; however, the higher temperature simultaneously enhanced the side reactions and thus led to a limited increase in product yield and DS.

When the molar ratio was 3 and the reaction temperature was 80 °C, prolonging the reaction time from 2 to 4, 6, and 8 h led to a slight decrease in yield from 87.2 to 84.5, 81.7, and 83.4%, and a slight decrease in DS from 0.62 to 0.61, 0.61, and 0.60, respectively (Fig. 1c). This suggested that a period of 2 h was affordable to perform the benzylation reaction, and a further increase in reaction time resulted in only more degradation of the product.



**Fig. 1.** Influence of (a) molar ratio, (b) reaction temperature, and (c) reaction time on the yield and DS of the benzylated bamboo

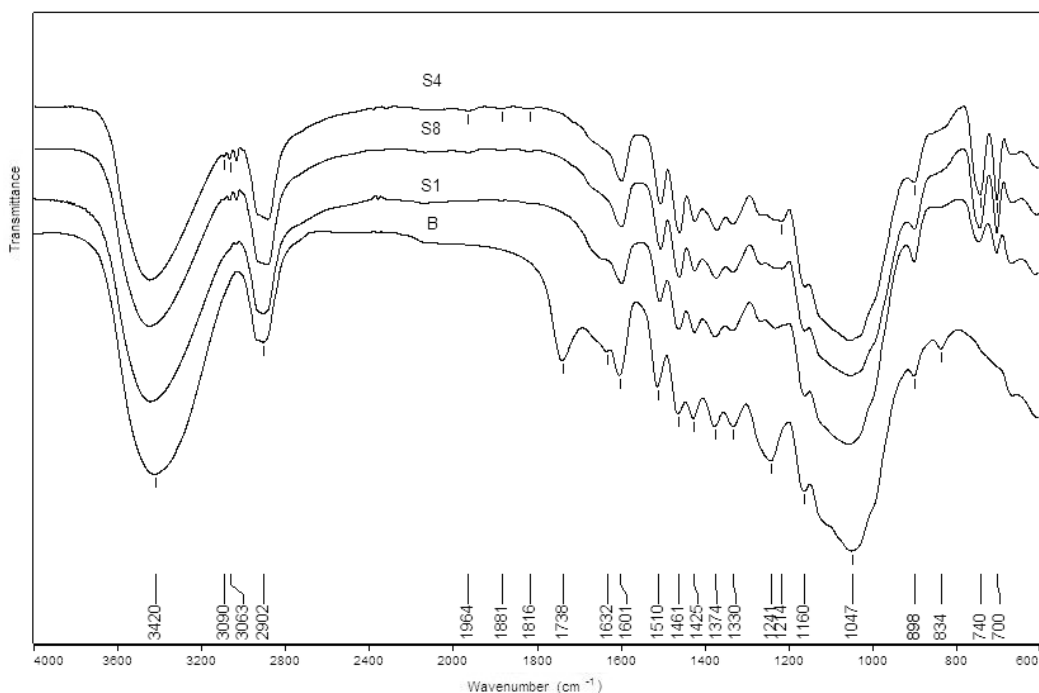
It was therefore suggested that the optimal conditions for benzylation of bamboo in NaOH/urea aqueous solution are a molar ratio of 3, a reaction temperature of 80 °C, and a reaction time of 2 h, which produced a yield of 87.2% and a DS of 0.62 of the

benzylated bamboo. This indicated that the milder reaction temperature (80 °C) could be used to benzylate bamboo in NaOH/urea aqueous solution as compared to the higher temperatures (100 and 120 °C) in the conventional concentrated NaOH aqueous solution (Kushwaha and Kumar 2011). The relatively lower temperature in the present study was probably due to the better swellability of cellulose as well as the diffusion and mobility of the reaction molecules in NaOH/urea aqueous solution (Qi et al. 2009).

### FT-IR Spectra Analysis

FT-IR spectra of benzylated bamboo samples with various DS (S1, S8, and S4) and the native ball-milled bamboo (B) are illustrated in Fig. 2. It can be clearly observed that the chemical structure of benzylated bamboo was significantly different from that of the native ball-milled bamboo. As a result of etherification, the intensity of the absorption band of hydroxyl groups at around  $3446\text{ cm}^{-1}$  diminished with an increase of substitution. As compared to the native ball-milled bamboo, the appearance of new absorption bands of phenyl groups located at  $740\text{ cm}^{-1}$  (aromatic C–H out-of-plane bending) and  $700\text{ cm}^{-1}$  (aromatic C–H angular deformation) indicated that the reaction of the mono-substitution of sodium ions by benzyl groups occurred (Djidjelli et al. 2008).

Evidently, from S1 to S4, the characteristic peaks of the benzyl groups become more intense with an increase in substitution. The triplet peaks at  $1964$ ,  $1881$ , and  $1816\text{ cm}^{-1}$ , corresponding to out-of-plane deformation vibrations of adjacent hydrogen from mono-substituted aromatic rings, appeared at benzylated bamboo with a high substitution (S4) (Pereira et al. 1997). In addition, the appearance of signals between  $3090$  and  $3063\text{ cm}^{-1}$  was related to aromatic C–H deformation and also observed in the highly benzylated samples (S8 and S4).



**Fig. 2.** FT-IR spectra of the benzylated bamboo with various substitutions (S1, S8, and S4) as compared to the native ball-milled bamboo (B)

A reduction in the absorption band at  $1730\text{ cm}^{-1}$  that corresponded to acetyl and carbonyl groups in the lignin and hemicelluloses was well detected for the benzylated sample, as compared to the native ball-milled bamboo (Li et al. 2010). This decrease was probably due to the fact that in the alkali medium, the acetyl groups were easily cleaved and the carboxyl groups reacted with NaOH to form carboxylates (Hon and Ou 1989). As a result, the absorption shifted from  $1730$  to  $1596\text{ cm}^{-1}$ . All the results above strongly support the incorporation of benzyl groups onto bamboo after modification. The benzylated bamboo with a high DS had a high proportion of non-polar benzyl groups. The incorporation of large non-polar benzyl groups resulted in better processability of bamboo particle as well as higher interfacial adhesion between bamboo particle and other hydrophobic particles/fibers. The increase of the interfacial interaction with hydrophobic polymer matrices increased the mechanical properties of the fiber composites (Zhang et al. 2005). For instance, it can be used as filler for the preparation of reinforce poly (vinyl chloride) composites.

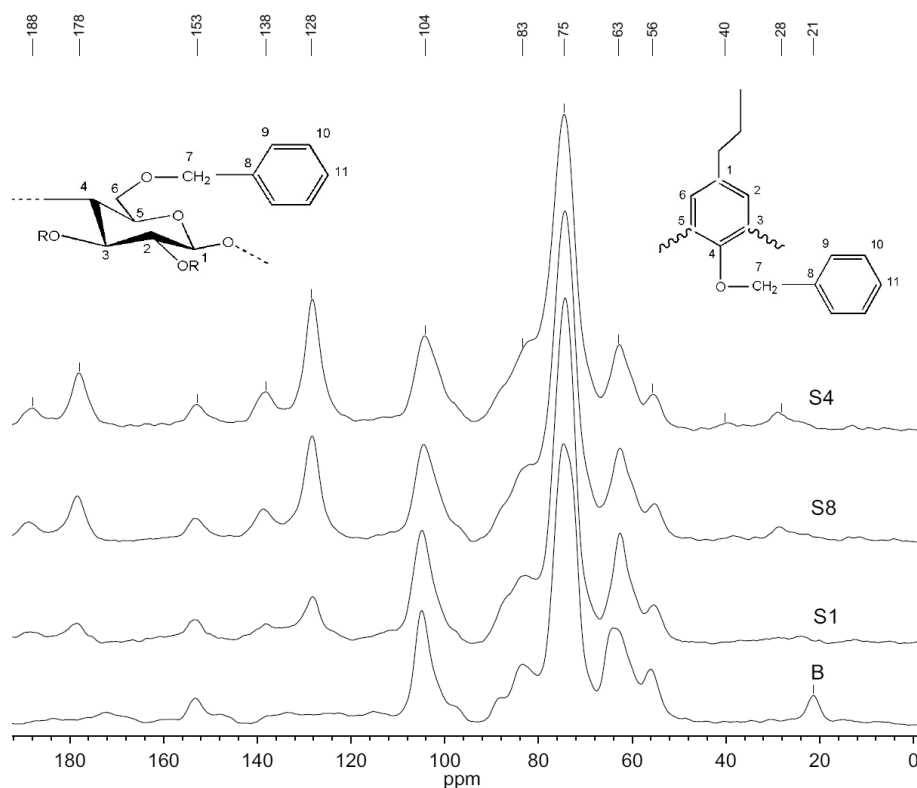
### CP/MAS $^{13}\text{C}$ -NMR Spectra Analysis

Solid state  $^{13}\text{C}$  CP/MAS NMR spectroscopy has been extensively applied to investigate lignocellulosic materials and their derivatives. The spectra of benzylated bamboo preparations with various DS (S1, S4, and S8) as well as the native ball-milled bamboo (B) are shown in Fig. 3. The signals that correspond to cellulose were observed at 63 ppm (C6), 75 ppm (C2, C3, and C5), 83, 87 ppm (C4), and 104 ppm (C1) (Popescu et al. 2010). It has been reported that xylans have signals at 102 ppm (C1), 84 ppm (C4), 72 to 75 ppm (C2 and C3), and 65 ppm (C5) (Wallace et al. 1995); however, these signals were overlapped with the strong signals of cellulose. In addition, the less intense signals at 56 ppm, 115 to 130 ppm, and 152 to 156 ppm, correspond to methoxyl and aromatic groups of lignin.

Obviously, the intensity of signals corresponding to the benzyl groups increased with the degree of substitution. The intense signal at 128 ppm is assigned to C9, C10, and C11 of benzyl groups substituted to the C6 position of cellulose, whereas the signal at 138 ppm is attributed to C4 on the benzylated lignin units, i.e., *p*-hydroxyl, guaiacyl, and syringyl (Ma 2007). The sharp signal at 171 ppm corresponds to the carbonyl groups.

The signal at 87 ppm obviously decreased after benzylation, and this is assigned to C4 of the amorphous region of cellulose. In the higher substituted sample, the intensity of signals at 87 ppm and 63 ppm, which correspond to the crystalline region of C4 and C6 in cellulose, were reduced markedly with an increase in substitution. The intensity of the signal at 104 ppm (C1 in cellulose) also decreased. These data indicate that the crystalline structure of cellulose was disrupted with increasing degree of substitution, which was in agreement with the X-ray diffraction analysis afterwards. The variation of the chemical shift and signal intensity was attributed to the basicity in the synthesis process. In the process of freezing and vigorous stirring, hydrogen bonds between cellulose layers were partially cleaved (Cai and Zhang 2005), thus activating the hydroxyl groups of the glucose units. In addition, the subsequent benzylation reaction resulted in the incorporation of large molecular groups, which made the whole lignocellulose looser.





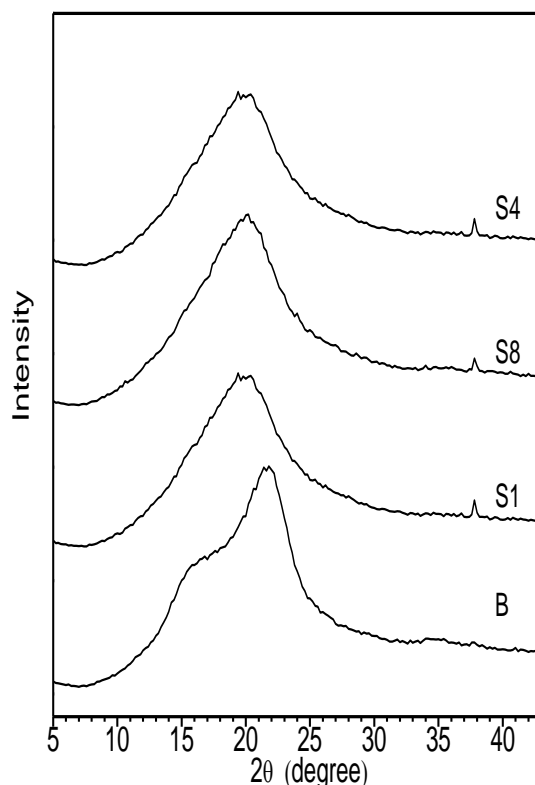
**Fig. 3.** CP /MAS  $^{13}\text{C}$ -NMR spectra of benzylated bamboo with various substitutions (S1, S8, and S4) as compared to the native ball-milled bamboo (B)

### X-ray Diffraction Analysis

Hydrophobic benzyl chloride was expected to disassemble the native structure of the bamboo via reacting with the active hydrophilic hydroxyl groups in the bamboo during the benzylation process. In order to investigate the crystal structure changes after benzylation, X-ray diffraction patterns of the benzylated bamboo were recorded as illustrated in Fig. 4. The native ball-milled bamboo exhibited a typical cellulose I pattern with reflections at  $2\theta=21.9^\circ$  and  $2\theta=16.3^\circ$  (Li et al. 2010), which eventually transformed into a new pattern after benzylation. The reflection peak at  $2\theta=21.9^\circ$  was found to shift towards  $2\theta=19.7^\circ$ , and the reflection peak at  $2\theta=16.8^\circ$  disappeared. The new scattering curve in the benzylated samples became lower in intensity and broader in width with an increased degree of substitution.

The calculated CrI values were 35.6, 36.3, and 36.8% for samples S1, S8, and S4, respectively. Obviously, there was negligible increase in the CrI with increased DS and yield of the product; however, these CrI values were lower than that of the native ball-milled bamboo (39.3%). This indicated that cold NaOH/urea aqueous solution pretreatment resulted in a decrease of crystallinity, whereas the degree of benzylation influenced the crystallinity slightly. It is well known that the alkaline treatments widen the lattice, change the conformation, and shift the lattice plane of cellulose. The most complete transformation of cellulose I to cellulose II can be achieved with NaOH treatment, while other alkalis, such as KOH and LiOH, produce only partial transformation. The slight increase trend in the present study was different from conventional benzylation (in

concentrated NaOH solution) (Deraman et al. 2001), however, in agreement with the results of homogeneous benzylation of cellulose in DMSO/TBAF. During the homogeneous benzylation process, it has also been reported that the crystallinity increases with increased substitution (Ramos et al. 2005). The benzylated bamboo with low crystallinity had improved thermoplasticity, thus it was a meltable material for further processing. For instance, binding of them with other particles or fibers may be easily operated by heating.



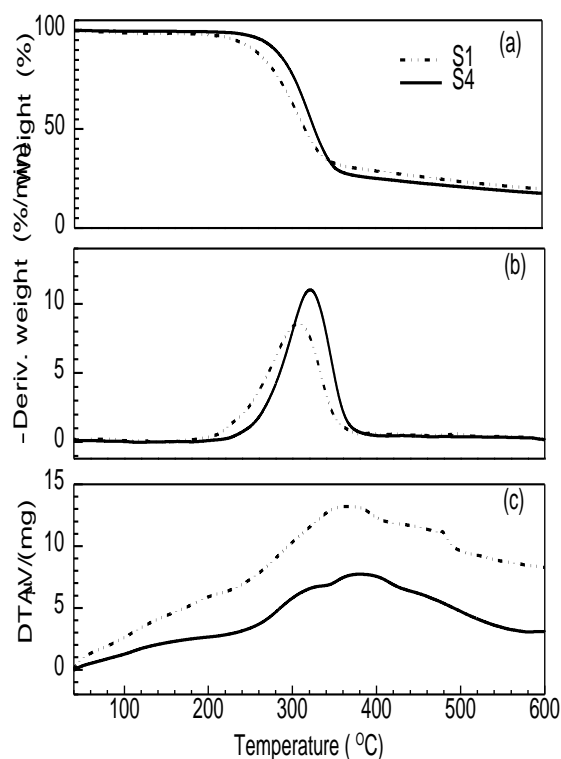
**Fig. 4.** X-ray diffraction patterns of benzylated bamboo with various substitutions (S1, S8, and S4) as compared to the native ball-milled bamboo (B)

It was suggested that the decrease in crystallinity resulted from both benzylation and the removal of the amorphous components. The decrystallization facilitated the thermoplasticity of lignocellulose by breaking the hydrogen bonds between the cellulose molecules. The large benzyl groups that were introduced into the cellulose brought in more free volume and resulted in the change of the supra-molecular structure of bamboo.

### Thermal Analysis

Thermal properties of benzylated bamboo with low (S1) and high (S4) DS were characterized with TGA and DTA measurements in an N<sub>2</sub> atmosphere. The TGA, DTG and DTA curves are shown in Fig. 5. As seen from the TG curves (Fig. 5a), the thermal degradation process of benzylated bamboo can be divided into three stages. In the initial stage, there was negligible weight loss below 200 °C for the two samples. Subsequently, the major degradation corresponding to softening and melting occurred with a further elevation of temperature (Liu et al. 2008). From the DTG plot (Fig. 5b), it can be

observed that the major thermal degradation of S1 commenced at 206 °C followed by a significant weight loss with an elevation of temperature to 371 °C. Whereas sample S4 decomposed thermally at a higher temperature of 232 °C and the rate of degradation kept rapid until the temperature was raised to 391 °C. The maxima degradation rate reached 8.5%/min at 307 °C and 11.7%/min at 320 °C for S1 and S4, respectively. Evidently, the benzylated bamboo with a higher DS underwent thermal degradation at the higher temperature. In the last stage, the depolymerization of the preparations terminated with the production of carbon, since the reactions occurred under an N<sub>2</sub> atmosphere. These results indicated that the thermal stability increased with the degree of substitution, which were similar to those described by Hon who studied the effect of modification of wood with thermal analysis methods (Zhang et al. 2005). It should be noted, however, that the thermal stability of benzylated bamboo was lower than that of the cellulose component, which began to be degraded at the higher temperature (above 300 °C as usual) (Li et al. 2010).



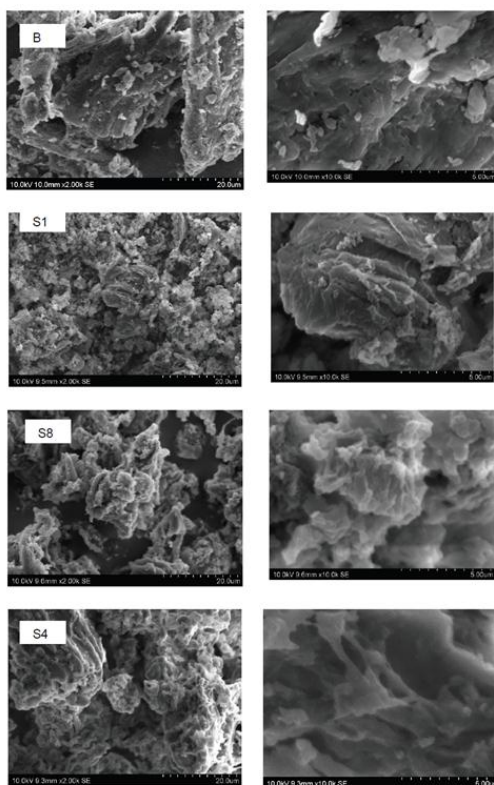
**Fig. 5.** TG, DTG, and DTA of benzylated bamboo with various substitutions (S1 and S4)

The reduction in the number of hydroxyl groups after benzylation also resulted in a decrease in the absorbed water content. This was evidenced by monitoring the changes in the endothermic peak of the DTA curves at around 100 °C (Fig. 5c). Benzylated bamboo S1 with a low DS displayed a high endothermic peak. This was because benzylated bamboo S1 had more hydroxyl groups, and it thereby had more absorbed water. However, no obvious peak was observed in the DTA curve around 100 °C for sample S4 with a high DS, due to its low amount of hydroxyl groups. The minor exothermic peak at around 300 °C should be attributed to the degradation of benzyl

groups in the benzylated bamboo, which produced low-molecular weight volatiles during the degradation process. The major exothermal peak shifted from 365 to 382 °C with an increase of DS from 0.31 (S1) to 0.74 (S4).

### SEM Examination

The SEM pictures of the benzylated bamboo with various DS (S1, S8, and S4) and the native ball-milled bamboo (B) are shown in Fig. 6, with enlargements of 2000 on the left and 10,000 on the right. As seen, the benzylated bamboo samples showed certain aggregation. As compared to the native ball-milled bamboo, the surfaces of benzylated bamboo preparations, even the sample with the lowest DS (S1), were completely disintegrated, and the well-defined edges were drastically lost. These results indicated that the benzylation reaction in the NaOH/urea aqueous solution changed the surface more effectively than the conventional way, since the previous observations of benzylated wood showed that rigid fiber still existed in the thermo-plasticized sample (Ma 2007). This was probably due to the fact that during the cold NaOH/urea system pretreatment and benzylation processes, the cold NaOH/urea aqueous solution disrupted the intermolecular and intramolecular hydrogen bonds effectively, and thus the crystalline structure was destroyed, which was in agreement with the results of the XRD analysis. The benzylated bamboo products with an amorphous matrix were easily melted and more compatible with non-polar polymers, i.e., PP (Danyadi et al. 2010), which have promising processability as a feedstock for composites.



**Fig. 6.** SEM images of benzylated bamboo with various substitutions (S1, S8, and S4) as compared to the native ball-milled bamboo (B)

## CONCLUSIONS

1. Bamboo was successfully benzylated in a 7% NaOH/12% urea aqueous solution under various reaction conditions. It was found that benzylation can be accomplished at a relatively low temperature as compared to the conventional way. Under the optimal conditions, i.e., a molar ratio of 3, a reaction temperature of 80 °C, and a reaction time of 2 h, a yield of 87.2% and a DS value of 0.62 of the benzylated bamboo were obtained.
2. The incorporation of benzyl groups into bamboo was evidenced by FT-IR and NMR spectroscopy. XRD analysis and SEM observation clearly showed that the crystalline structure of the native ball-milled bamboo was damaged after benzylation modification. Furthermore, the benzylated bamboo underwent thermal degradation at a higher temperature with an increase of substitution.
3. The benzylated bamboo obtained had a low crystallinity as well as large non-polar groups and was potential filler applicable in the composite material industry.

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