

## Solvent-free acetylation of bacterial cellulose under moderate conditions

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### ARTICLE INFO

#### Article history:

Received 16 July 2010

Received in revised form 6 October 2010

Accepted 7 October 2010

Available online 15 October 2010

#### Key words:

Bacterial cellulose

Acetylation

Iodine

Hydrophobic

### ABSTRACT

Bacterial cellulose preserving the microfibrillar morphology was partially acetylated by the solvent-free acetylation method using acetic anhydride in the presence of iodine as a catalyst. The results showed that within the range of catalyst amounts studied, the overall degree of substitution increased as the amount of iodine used increased. We also found that the reaction time and temperature had an active influence on the extent of acetylation. X-ray diffraction profiles indicated that acetylation proceeded from the surface to the interior of BC nanofibers, and scanning electron microscopy images revealed that even low levels of acetylation were effective to make the nanofibers separated from each other. NMR analysis indicated the regio-nonspecific reactivity of the OH groups in the glucose units in the acetylation process. The obtained acetylated BC membrane shows more hydrophobic surface and good mechanical properties which is in favor of enhancing the hydrophobic non-polar polymeric matrix.

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### 1. Introduction

Bacterial cellulose (BC) produced by bacteria as a renewable nanobiomaterial has attracted considerable attention in recent years because of its excellent physical properties (Iguchi, Yamanaka, & Budhiono, 2000). It has an ultra fine network of cellulose nanofibers with a high Young's modulus of up to 138 GPa, a tensile strength of 2 GPa and thermal expansion of only  $0.1 \times 10^{-6} \text{ K}^{-1}$  (Page & Elhosseiny, 1983; Sakurada, Nukushina, & Ito, 1962), which are extremely attractive for applications as reinforcement in composites (AziziSamir, Alloin, & Dufresne, 2005; Eichhorn, Dufresne, Aranguren, et al., 2010; Nishino, Matsuda, & Hirao, 2004; Nogi, Abe, et al., 2006; Nogi, Ifuku, et al., 2006; Yano et al., 2005). The fact that it is biodegradable and light-weight makes it very attractive for the future industrial purposes. Therefore, various efforts have been made to investigate the BC reinforced polymer composites. Gindl and Keckes (2004) produced cellulose acetate butyrate composites which were reinforced by 10.3 vol.% BC with the Young's modulus of 3.2 GPa and tensile strength of 52.6 MPa, respectively. While the Young's modulus and tensile strength of composite with 32 vol.% bacterial cellulose was 5.8 GPa and 128.9 MPa, respectively. Yano et al. (2005) processed bacterial cellulose reinforced acrylic resin and epoxy resin composites. Due to the size effect, the nanofibre network led to a very low loss of transparency even at high fibre content. While the mechan-

ical properties of the BC/epoxy resin composite is significantly improved by reinforcing with 65 wt.% bacterial cellulose.

Although the BC nanofibrils have a great potential as mentioned above, it cannot be easily dispersed homogeneously in the hydrophobic non-polar polymeric matrix due to their high surface and hydrophilic nature. Besides, the hygroscopicity of cellulose causes dimensional instability of the composites. The hydrophilic behavior of cellulose is attributed to the hydroxyl groups that are located on the surface of the cellulose fibers. Several methods have been proposed to overcome this problem recently involving the chemical modification of the cellulose surface hydroxyl groups with various reagents (Fabbri, Champon, Castellano, Belgacem, & Gandini, 2004; Gousse, Chanzy, Cerradab, & Fleury, 2004; Hafren, Zou, & Cordova, 2006; John, Franci, Varughese, & Thomas, 2008; John & Anandjiwala, 2008; Siró & Plackett, 2010). Among the different modification methods, acetylation is a kind of commonly used chemical modification, where the hydroxyl groups of cellulose are replaced by less hydrophilic acetyl groups (Nogi, Abe, et al., 2006; Nogi, Ifuku, et al., 2006; Wu et al., 2004). Until now, largest amount of acetylated BC is produced by the so-called "acetic acid process". In this process, BC is first swelled in acetic acid and then acetylated with acetic anhydride in the presence of sulfuric acid or perchloric acid as catalysts. Despite the advantages of low cost and high productivity, serious degradation of the cellulose and hydrolysis of cellulose acetate inevitably occur because of the water used and remaining acid catalysts in the quenching step (Biswas et al., 2007). During recent years, it has been reported that polysaccharides such as cellulose, starch, chitosan can be successfully esterified with the applications of iodine as a Lewis acid catalyst (Ahmed & van Lier, 2006; Biswas, Shogren, & Willett, 2005; Biswas et al., 2008;

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Phukan, 2004; Ren, Sun, Liu, Cao, & Luo, 2007), which is cheap, convenient, environment friendly and cost-effective. To our knowledge, this reaction has not been exploited for the modification of BC nanofibers. Accordingly, in this study, we examined the acetylation of BC by employing the acid anhydride/iodine system under moderate conditions. In addition, we explored the effects of reaction temperature, reaction duration, and iodine concentration on the extent of acetylation and found the optimal reaction conditions to produce acetylated BC in a more economical and environmentally friendly way.

## 2. Experimental

### 2.1. Materials

BC membrane was kindly provided by Hainan Yeguo Foods Co. Ltd. The membrane was washed with distilled water and treated with 1% sodium hydroxide at 80 °C for 1 h, followed by rinsing with water. The other chemicals were purchased from Shanghai Chemical Company and were used as received without any further purification.

### 2.2. Acetylation of BC

Several pieces of water-wet samples containing about 400 mg dry cellulose each piece were dried for 2 h at 80 °C. The sample was then placed in a 50 mL three-necked flask fitted with a mechanical stirrer containing a mixture of 20 mL of acetic anhydride and different concentrations of iodine (0.05, 0.75, 0.1, 0.125, 0.15 mM). The mixture was heated to 60, 70, 80, 90 and 100 °C and left for 15, 30, 60, 120 min at 80 °C. At the end of every experiment, the flask was cooled to room temperature. A saturated sodium thiosulfate solution was added to the flask and stirred until the mixture color changed from dark brown to colorless, indicating the transformation of iodine to iodide. Then the BC sample piece maintaining its original appearance was washed thoroughly with 75% (v/v) alcohol followed by distilled water to remove the byproducts and remaining reagents. Samples were dried in a vacuum oven at 60 °C for 12 h.

### 2.3. Characterization

The determination of the degree of substitution (DS) was conducted by back titration method according to the report (Sanios, Dart, & Dawkins, 1997). The morphologies of acetylated and untreated BC membranes were characterized using S-4800 field emission scanning electron microscope. Prior to analysis, samples were cut into small pieces from the prepared sample, and coated with a thin layer of evaporated gold. X-ray diffractometry in reflection mode was carried out over a range of 2–70° using a D/Max-2550 PC with Cu K $\alpha$  radiation. The infrared spectra of acetylated and untreated BC membranes were recorded on a Nicolet NEXUS-670 FTIR. Each sample was grounded with dried potassium bromide (KBr) powder and compressed into a disc, and then was subjected to analysis. Thermal gravimetric (TG) curves were obtained for dried samples in Universal V3.8B equipment from TA-Instruments. Samples were heated in open alumina pans from 30 to 500 °C, under a nitrogen atmosphere, at a heating rate of 20 °C/min. Solid-state cross polarization magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS <sup>13</sup>C NMR) spectra were recorded using a Bruker AV400 spectrometer operated at 100 MHz with 5 mm MAS BBO probe at ambient temperature. The water contact angle, an indicator of the wettability of surfaces, was measured at room temperature using a contact angle goniometer (OCA40, Dataphysics, Germany). Membranes of native BC and acetylated BC were prepared and oven-dried at 80 °C for

**Table 1**

The DS of acetylated BC obtained under different conditions.

Acetylation conditions			Acetylated cellulose	
T (°C)	t (min)	Iodine (mM)	Sample no.	DS
60	60	0.125	1	0.23
70	60	0.125	2	0.87
80	60	0.125	3	1.75
90	60	0.125	4	–
100	60	0.125	5	–
80	15	0.125	6	0.45
80	30	0.125	7	0.65
80	60	0.125	3	1.75
80	120	0.125	8	1.98
80	60	0.05	9	0.73
80	60	0.075	10	1.12
80	60	0.1	11	1.52
80	60	0.125	3	1.75
80	60	0.15	12	–

24 h. A droplet of distilled water was deposited onto the surface of the membranes. The contact angle was measured on 5 different points and the average values were calculated. Tensile strengths of both native and acetylated BC membranes were measured using a WDW 3020 Universal Testing Machine at room temperature and a crosshead speed of 5 mm/min. Elongation at break and Young's modulus of these samples were, therefore, measured. Samples with 30 mm in length, 5 mm in width and 0.03 mm in thickness were used in these measurements.

## 3. Results and discussion

### 3.1. Optimization of the reaction temperature and time

The reaction conditions were optimized using the following process: 400 mg cellulose, 20 mL acetic anhydride and 0.125 mM iodine were mixed in a 50 mL three-necked flask fitted with a mechanical stirrer. Different reaction time and temperatures were used. The DS were determined by back titration method for each product (Table 1). The samples were acetylated by increasing the reaction temperature from 60 °C to 100 °C at different time periods, as shown in the first list in Table 1. It was found that the DS of the sample were higher as the temperature increased. While when the BC was acetylated over 90 °C, the BC membrane could not maintain its original appearance and integrity. Therefore, the temperature at 80 °C was selected. Then, under the fixed conditions of reaction temperature, the DS of the corresponding samples increased when the reaction time was changed from 15 to 120 min. However, considering the degradation of cellulose and hydrolysis of cellulose acetate at long reaction time, an optimized reaction time of 60 min was selected. Therefore, the optimum condition was that the cellulose was acetylated at 80 °C for 60 min.

Meanwhile, the results clearly indicated that the reaction temperature and time played important roles in the process of acetylation. The DS increased when the reaction time was extended and the temperature increased. It was proposed that the cellulose nanofibers were acetylated inhomogeneously, that is, at the beginning of the reaction, the BC will go through rapid surface acetylation, and as the acetylation progressed, the inside of the cellulose nanofiber was acetylated slowly with the collapsing crystal structure of cellulose I (Ifuku et al., 2007). In addition, the high temperature increased the swelling ability of cellulose and the diffusion rate of acetic anhydride and iodine significantly. However, the higher temperature and longer time would result in the hydrolysis of the ester groups and/or the decomposition of cellulose backbones, furtherly destroy the original appearance of the BC

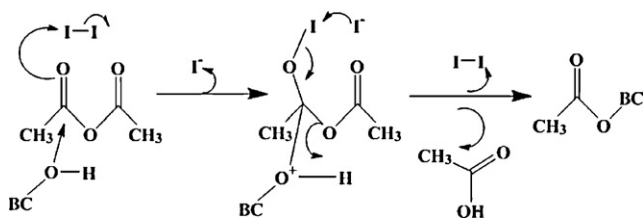


Fig. 1. The mechanism of BC acetylated by using iodine as the catalyst.

membranes (Li, Zhang, et al., 2009; Li, Chen, et al., 2009; Satgé et al., 2002).

### 3.2. Effects of iodine quantities

The effect of iodine concentration on the extent of acetylation was studied by adding a series of different concentration of iodine (0.05, 0.75, 0.1, 0.125, 0.15 mM) to a mixture which contained 400 mg cellulose and 20 mL acetic anhydride. The mixtures were treated under the optimum conditions in which the cellulose samples were acetylated at 80 °C for 60 min. The DS are shown in the third list in Table 1. The general mechanism is outlined in Fig. 1. In the reaction process, iodine first activates the carbonyl carbon of acetic anhydride in the presence of alcoholic groups, as the oxygen of R-OH attacks the carbonyl carbon resulting in  $sp^3$  hybridization. The acetic anhydride reacts with hydroxyl groups involving a nucleophilic attack on the acyl carbon center of the acetic anhydride molecule by a lone pair of the alcoholic hydroxyl group followed by subsequent loss of acetic acid to generate the ester (Biswas et al., 2005; Hill, Jones, Strickland, & Centin, 1998). The acetic ester of the respective alcohol formed through the reaction of the iodide ion

with the iodine atom that attached to the oxygen of the carbonyl group, resulting in free iodine. At the end of the reaction, addition of a saturated aqueous solution of sodium thiosulfate removes all the free iodine. As shown in the third list in Table 1, the DS of the products increased with the increasing concentration of iodine, which can be attributed to more acetic anhydride–iodine intermediates, and thus cellulose was more easily acetylated. By increasing the concentration of iodine from 0.05 to 0.125 mM, the DS of products increased up to 1.75. At higher concentration of iodine, destruction of the appearance of the BC sample was observed, and could be attributed to its degradation.

### 3.3. FT-IR spectra

Fig. 2 shows the FT-IR spectra of BC and acetylated BC samples. The bands at 3410, 2900, 1648, 1426, 1372 and 1060  $cm^{-1}$  in Fig. 2a are associated with native BC (Barud, de Araújo Júnior, et al., 2008; Barud, Barrios, et al., 2008; Li, Zhang, et al., 2009; Li, Chen, et al., 2009). In comparison, the characteristic vibrations of the grafted acetyl groups were easily identified in the FT-IR spectra of modified nanofibers: namely the carbonyl C=O stretching vibration at 1755  $cm^{-1}$  (C=O), the methyl in-plane bending in  $-O(C=O)-CH_3$  at 1372  $cm^{-1}$  (C-H), and the C-O stretching of acetyl group at 1237  $cm^{-1}$  (C-O) (Çetin et al., 2009). Another important aspect observed in the cellulose acetate spectrum is the decreasing absorption intensity of the band located at around 3410  $cm^{-1}$  assigned to the stretching of the hydroxyl group when compared with BC. This decreasing phenomenon occurs because the hydroxyl groups in BC are partially substituted by acetyl groups in the reaction. In addition, no absorption was observed in the region between 1840 and 1760  $cm^{-1}$  in the spectra. It demonstrated that the product was free of unreacted acetic anhydride. The absence of absorp-

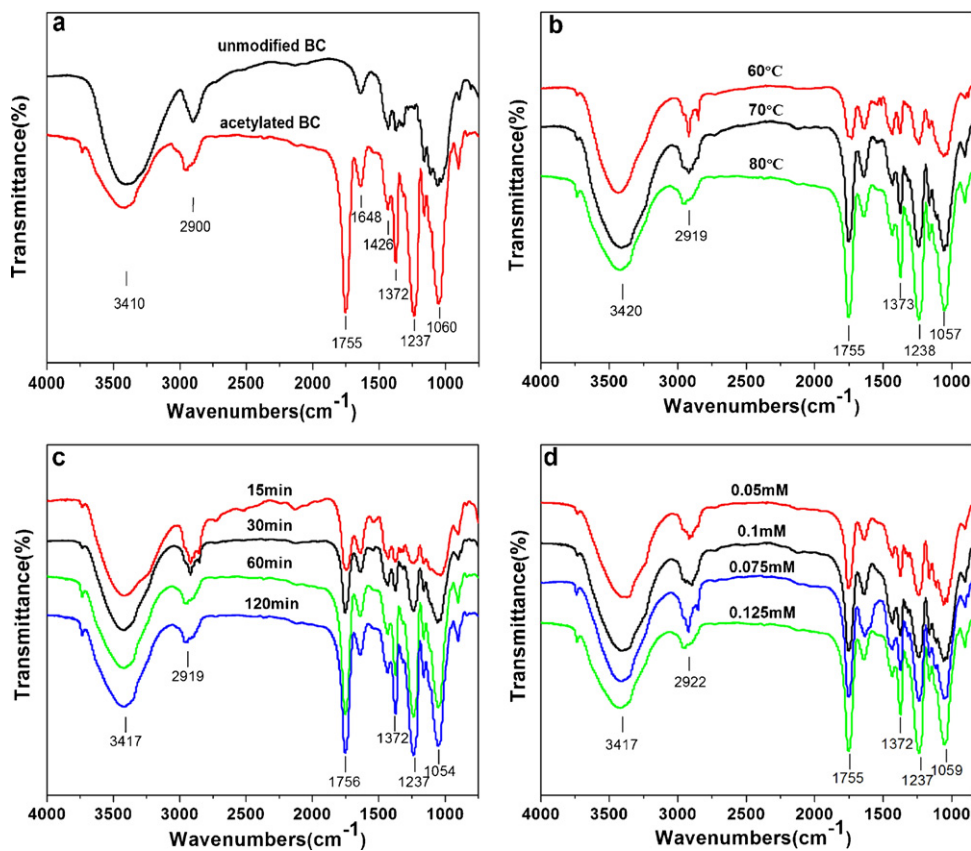


Fig. 2. FT-IR spectra of (a) unmodified BC and acetylated BC sample 3 and acetylated BC samples prepared, (b) at different reaction temperatures (60 °C, 70 °C, 80 °C), (c) different reaction time (15 min, 30 min, 60 min, 120 min), and (d) different iodine concentrations (0.05 mM, 0.075 mM, 0.1 mM, 0.125 mM).

tion at  $1700\text{ cm}^{-1}$  attributed to carboxylic group indicated that the product was also free of any acetic acid byproduct (Adebajo & Frost, 2004). The effects of reaction time, reaction temperature, and iodine concentrations on the extent of acetylation were also investigated by the bands intensity of acetylated cellulose samples and their spectra are given in Fig. 2b–d. The intensity of these characteristic bands in three major bands of cellulose triacetate increased gradually with reaction time, reaction temperature and iodine concentration increased, indicating that nanofibers were increasingly modified. Though quantitative analysis of IR spectra is not possible because of variation in film thickness, the overall change in absorption band intensities is in good accord with the DS values from acetylation (Yamamoto, Horii, & Hirai, 2006).

### 3.4. WAXD spectra

The impact of chemical modification on the crystallinity and structure of the cellulose nanofibers was further evaluated using WAXD analysis. The diffraction profiles of unmodified and acetylated BC membranes are presented in Fig. 3. The native sample peaks localize at around  $14.6$ ,  $16.8$  and  $22.8^\circ$  are assigned to the characteristic interplane distances of cellulose  $I_\alpha$  and  $I_\beta$  phases (Maneerung, Tokura, & Rujiravanit, 2008; Hu et al., 2009). From XRD of BC samples with different DS, the halo located at approximately  $8^\circ$  is cited as the principal characteristic of semicrystalline acetylated derivative cellulose. The position of this peak indicates the generation of a disorder when BC was acetylated. The disorder is caused by the projection of the substituting groups (acetyl groups) along the axes and is associated with an increase in the interfibrillar distance and the breakdown of microfibrillar structures (Barud, de Araújo Júnior, et al., 2008; Barud, Barrios, et al., 2008; Filho et al., 2000). The acetylated cellulose presents a low degree of crystallinity compared with that of the original cellulose due to the substitution of the hydroxyl groups by acetyl groups with greater volume, which broke the inter- and intra-molecular hydrogen bonds of cellulose. The diffraction patterns of the DS 0.45

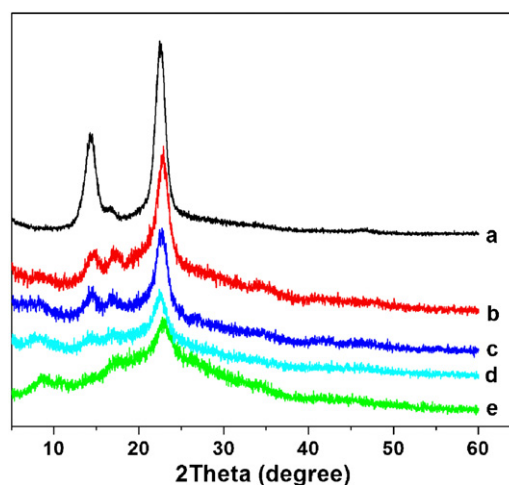


Fig. 3. The XRD patterns of (a) native BC and acetylated cellulose, (b) sample 6 (DS 0.45), (c) sample 7 (DS 0.65), (d) sample 3 (DS 1.75) and (e) sample 8 (DS 1.98).

and 0.65 samples seem to almost agree with that of the untreated sample, indicating that nanofibers maintained their original crystalline structure. This result indicated that easily accessible surface hydroxyl groups were first modified. On the other hand, with the increasing number of hydroxyl groups being substituted, the DS 1.75 and 1.98 samples with longer reaction time had smaller diffraction peaks from cellulose I than those in the untreated and DS 0.45 and 0.65 samples, indicating that the inner crystalline regions were increasingly modified by the reaction progress. These results may support the presumption that the present acetylation proceeds from the surface to the core of each microfibril with the increase of reaction time, and the crystal structure of the nanofibers changed with the increase of acetyl DS, similar to the case in the previous report (Sassi, Tekely, & Chanzy, 2000).

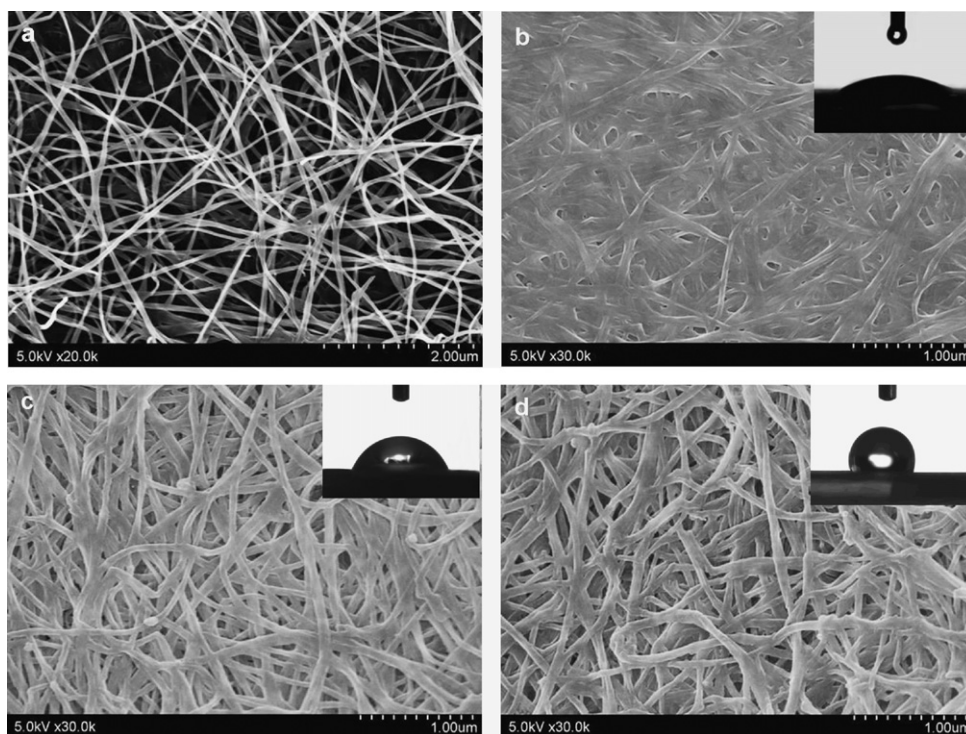


Fig. 4. FE-SEM images of untreated BC (a) freeze-dried, (b) vacuum-dried and vacuum-dried acetylated BC samples, (c) sample 7 (DS 0.65) and (d) sample 3 (DS 1.75). The insets show the profile of water droplets on the membrane surface.

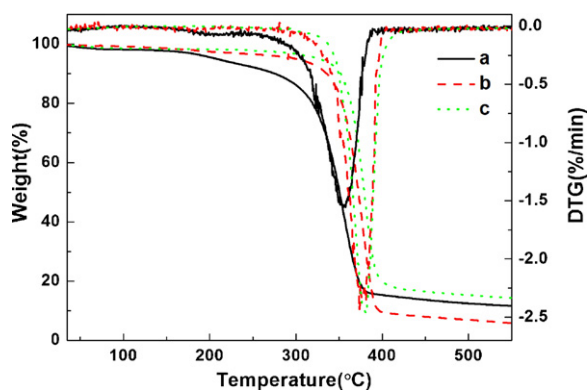


Fig. 5. TG and DTG curves of (a) BC and acetylated BC, (b) sample 2 and (c) sample 3.

### 3.5. Surface morphology and wettability

The morphology of BC nanofibers before and after acetylation was studied using FE-SEM. Fig. 4 shows the FE-SEM images of original freeze-dried and vacuum-dried BC membranes and vacuum-dried acetylated samples. The images show the microfibrillar structure of cellulose and aggregates of semicrystalline extended-cellulose chains in an ultrafine network structure. It consists of continuous nano-fibers with a diameter in the range from 20 to 60 nm. From Fig. 4a and b, we can see that the surfaces of non-acetylated fibers are rather smooth and clean, while the acetylated fibers from Fig. 4c and d are rougher, indicating that acetylation has affected the structure. Moreover, a swollen morphology of the acetylated fibers was observed which could be due to the chemical treatment in solvent media. It was also observed that the microfibrils of vacuum-dried BC are seen to be densely coagulated shown in Fig. 3b with the imperceptible interstitial cavities due to the hydrophilicity of cellulose and the strong surface tension of water. In contrast to this, the acetylated BC nanofibers are separated from each other. This change is considered to result from increased hydrophobicity of the acetylated surfaces. On the other hand, the volume of nanofibers in DS 1.75 sample obviously increases as shown in Fig. 4d. This change in volume also indicates that bulky acetyl groups were heterogeneously introduced to the inside of nanofibers after the surface reaction (Ifuku et al., 2007).

Water wetting images on BC surface at equilibrium before and after acetylation treatment are shown in the insets of Fig. 4. The average water contact angles for the native and acetylated BC sample 7 and 3 were 18.2, 76.7 and 112.1, respectively. The results show that the acetylation changed the surface characteristics of the nanofibers from highly hydrophilic to more hydrophobic. As expected, water wettability decreased drastically after acetylation, which further confirmed that the chemical modification had indeed occurred at the surface of BC samples. The obtained acetylated BC membrane with hydrophobic surface indicated good compatibility with hydrophobic non-polar polymeric matrix (Nogi, Abe, et al., 2006; Nogi, Ifuku, et al., 2006).

### 3.6. Thermal analysis

The thermal properties of unacetylated BC and acetylated BC samples 2 and 3 are illustrated in Fig. 5. As shown in Fig. 5, the TGA curves of unacetylated cellulose and acetylated cellulose are very similar, which can be distinctly divided into three stages: During the initial stage from room temperature to 120 °C, the water and other residue solvent vaporized. In Fig. 5, from room temperature to 120 °C, the TGA thermogram of unacetylated cellulose displayed a minor weight loss which is attributed to water desorp-

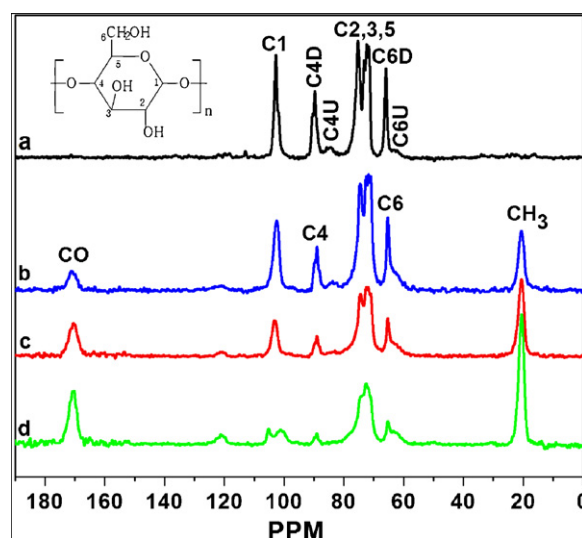


Fig. 6. The CP/MAS  $^{13}\text{C}$  NMR spectra of (a) native BC and acetylated BC, (b) sample 6 (DS 0.45), (c) sample 3 (DS 1.75) and (d) sample 8 (DS 1.98).

tion. However, this minor loss of weight is not obvious for the two acetylated BC samples; that is to say, the acetylated samples are more hydrophobic than the native cellulose. From 220 to 390 °C, the crystalline region started to destruct and the polymer simultaneously decomposes, which evidently resulted in amorphous structure increases and the degree of polymerization decreases. During this stage from 390 to 550 °C, the crystalline region has been completely destructed and the cellulose decomposed into monomer of D-glucopyranose, which could be further decomposed into free radical (Antal & Varhegyi, 1995; Yang, Xu, Ma, & Wang, 2008).

The onset thermal degradation temperatures were considered to start at 293 °C for unacetylated cellulose, 326 °C for sample 2, and 342 °C for sample 3, and the highest rate of weight loss of native cellulose occurred at 356 °C, while sample 2 and sample 3 happened at 374 and 381 °C, respectively. This increasing trend of decomposition temperature indicated that the thermal stability of the acetylated BC is higher than that of untreated BC.

### 3.7. CP/MAS $^{13}\text{C}$ NMR spectra

The CP/MAS  $^{13}\text{C}$  NMR spectroscopy for BC and acetylated sample with different DS are shown in Fig. 6. In these spectra, the noticeable signals in the region between 50 and 110 ppm are attributed to the different carbons of cellulose. The carbons can be assigned as follows: C1 (105.2 ppm), C4 crystalline (C4D 89.0 ppm), C4 amorphous (C4U 84.3 ppm), C2/C3/C5 (72.6 and 74.8 ppm), C6 crystalline (C6D 65.3 ppm), and C6 amorphous (C6U 62.9 ppm) (Attala, Gast, Sindorf, Bartuska, & Maciel, 1980). After acetylation, two peaks appeared at 171.4 and 21.1 ppm in spectra b, c and d, are assigned to CO and CH<sub>3</sub> in acetyl group. It also confirms the success of acetylation.

The crystalline and disordered components were detected for C4 or C6 carbon, respectively. As can be observed from Fig. 6, the intensity of the signals at 89.0 ppm for crystalline C4 and 65.3 ppm for crystalline C6 decreased sharply in spectra c and d, which reveal that the crystalline structure of the cellulose was disrupted and the acetylation reaction occurs in the system. On the other hand, the intensities of C4 and C6 resonance lines decrease with the increase of DS, indicating the changes in crystalline and amorphous components in the samples. Finally, the increase of the intensity for CO and CH<sub>3</sub> indicated that the extent of acetylation increased, which is consistent with the trend of the DS in Table 1.

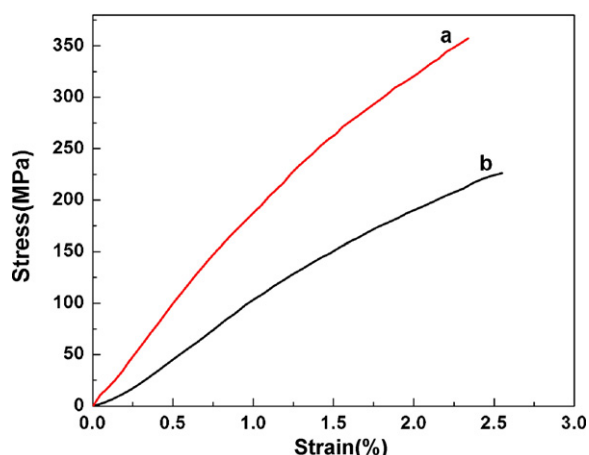


Fig. 7. Tensile stress–strain behaviors of air dried BC (a) and acetylated BC sample 3 (b).

In addition, the ordered and disordered components of cellulose, which are respectively detected as the C4D/C6D and C4U lines, have been found to decrease at almost the same rate with the increase of reaction time as shown in Fig. 6. This fact indicates that the respective OH groups associated with these carbons undergo acetylation almost simultaneously, irrespective of the differences in position in the glucose units and in structure between the ordered and disordered OH groups. This may be due to the three OH groups underwent acetylation at nearly the same time in a very thin layer produced at the boundary between the acetylated and nonacetylated regions and successively move from the surface to the inner part in each nanofibril (Yamamoto et al., 2006). Similar regio-nonspecific reactivity of the OH groups in the glucose units was also observed for acetylation of cellulose by the previous solid-state  $^{13}\text{C}$  NMR measurement (Sassi et al., 2000). Apparently, in Fig. 6d the peak representing C1 of acetylated BC has a peak resolved into two peaks which may be due to the oligomers crystallization resulting from the hydrolysis of the ester groups and/or the decomposition of cellulose backbones with the higher temperature and the longer time (Vanderhart, Hyatt, Atalla, & Tirumalai, 1996).

### 3.8. Mechanical properties

The tensile behaviour of native BC and acetylated BC membranes are shown in Fig. 7. The Young's modulus (20.8 GPa) and tensile strength (357.3 MPa) of BC are higher than the literature values of Young's modulus (16.9 GPa) and tensile strength (260 MPa), respectively (Iguchi et al., 2000). It is found that the Young's modulus (13.4 GPa) and tensile strength (225.8 MPa) of acetylated BC are lower than that of BC due to the lower degree of crystallinity and the less dense network structure. At the same time, the results also show that the acetylation of BC membranes does not result in a significant decrease in mechanical properties, so the acetylated BC membranes are suitable for the reinforcement in composites with non-polar polymeric matrix.

## 4. Conclusions

BC nanofibrils were easily acetylated under moderate conditions by reaction with acetic anhydride, in the presence of iodine as a catalyst. The DS of acetylation of cellulose was influenced by the reaction time and temperature, and the DS had an increasing trend with the increasing concentration of iodine. In our experimental conditions, the nanostructural morphology of the BC fibers was still preserved when the reaction was kept at temperature less

than 80 °C, for a time period of 60 min and using an iodine catalyst in an amount of less than 0.125 mM. The reaction time for 60 min and the temperature at 80 °C with the 0.125 mM iodine were the optimum condition in our work. By increasing the reaction time, the acetylation proceeded from the surface to the interior of BC nanofibrils, leading to a higher substitution, but also to a loss of crystallinity. Moreover, the acetylation process showed regio-nonspecific reactivity of the OH groups in the glucose units. The obtained acetylated BC membrane shows hydrophobic surface and good mechanical properties which is in favor of enhancing the hydrophobic non-polar polymeric matrix. It is concluded that the esterification reaction using iodine as catalyst was highly efficient, fast, economical and environmentally friendly which could be adopted on a commercial scale for the acetylation of BC. It is considered as a straightforward method to modify the surface of BC nanofibrils with various DS and opens up a new opportunity for using BC nanofibrils as reinforcement in non-polar polymer matrices.

## Acknowledgements

The authors thank Hainan Yeguo Foods Co. Ltd for supplying BC samples. This work was financially supported by Doctoral Fund of Ministry of Education of China (20090075120011), Programme of Introducing Talents of Discipline to Universities (B07024), Shanghai Leading Academic Discipline Project (B603) and Project of the Action on Scientists and Engineers to Serve Enterprises (2009CJE20016).

## References

- Adebajo, M. O., & Frost, R. L. (2004). Infrared and  $^{13}\text{C}$  MAS nuclear magnetic resonance spectroscopic study of acetylation of cotton. *Spectrochimica Acta – Part A: Molecular and Biomolecular Spectroscopy*, 60, 449–453.
- Ahmed, N., & van Lier, J. E. (2006). Molecular iodine in isopropenyl acetate (IPA): A highly efficient catalyst for the acetylation of alcohols, amines and phenols under solvent free conditions. *Tetrahedron Letters*, 47, 5345–5349.
- Antal, M. J., & Varhegyi, G. (1995). Cellulose pyrolysis kinetics: The current state of knowledge. *Industrial and Engineering Chemistry Research*, 34, 703–717.
- Attala, R. H., Gast, J. C., Sindorf, D. W., Bartuska, V. J., & Maciel, G. E. (1980).  $^{13}\text{C}$  NMR spectra of cellulose polymorphs. *Journal of the American Chemical Society*, 102, 3249–3251.
- AziziSamir, M. A. S., Alloin, F., & Dufresne, A. (2005). Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules*, 6, 612–626.
- Barud, H. S., de Araújo Júnior, A. M., Santos, D. B., de Assunção, R. M. N., Meireles, C. S., Cerqueira, D. A., et al. (2008). Thermal behavior of cellulose acetate produced from homogeneous acetylation of bacterial cellulose. *Thermochimica Acta*, 471, 61–69.
- Barud, H. S., Barrios, C., Regiani, T., Marques, R. F. C., Verelst, M., DexpertGhys, J., et al. (2008). Self-supported silver nanoparticles containing bacterial cellulose membranes. *Materials Science and Engineering: C*, 28, 515–518.
- Biswas, A., Selling, G., Appell, M., Woods, K. K., Willett, J. L., & Buchanan, C. M. (2007). Iodine catalyzed esterification of cellulose using reduced levels of solvent. *Carbohydrate Polymers*, 68, 555–560.
- Biswas, A., Shogren, R. L., & Willett, J. L. (2005). Solvent-free process to esterify polysaccharides. *Biomacromolecules*, 6, 1843–1845.
- Biswas, A., Shogren, R. L., Selling, G., Salch, J., Willett, J. L., & Buchanan, C. M. (2008). Rapid and environmentally friendly preparation of starch esters. *Carbohydrate Polymers*, 74, 137–141.
- Çetin, N. S., Tingaut, P., Özmen, N., Henry, N., Harper, D., Dadmun, M., et al. (2009). Acetylation of cellulose nanowhiskers with vinyl acetate under moderate conditions. *Macromolecular Bioscience*, 9, 997–1003.
- Eichhorn, S. J., Dufresne, A., Aranguren, M., Marcovich, N. E., Capadona, J. R., Rowan, S. J., et al. (2010). Review: Current international research into cellulose nanofibres and nanocomposites. *Journal of Materials Science*, 45, 1–33.
- Fabbri, P., Champon, G., Castellano, M., Belgacem, M. N., & Gandini, A. (2004). Reactions of cellulose and wood superficial hydroxy groups with organometallic compounds. *Polymer International*, 53, 7–11.
- Filho, G. R., Da Cruz, S. F., Pasquini, D., Cerqueira, D. A., Prado, V. D. S., & De Assunção, R. M. N. (2000). Water flux through cellulose triacetate films produced from heterogeneous acetylation of sugar cane bagasse. *Journal of Membrane Science*, 177, 225–231.
- Gindl, W., & Keckes, J. (2004). Tensile properties of cellulose acetate butyrate composites reinforced with bacterial cellulose. *Composites Science Technology*, 64, 2407–2413.

- Gousse, C., Chanzy, H., Cerradab, M. L., & Fleury, E. (2004). Surface silylation of cellulose microfibrils: Preparation and rheological properties. *Polymer*, *45*, 1569–1575.
- Hafren, J., Zou, W. B., & Cordova, A. (2006). Heterogeneous 'organoclick' derivatization of polysaccharides. *Macromolecular Rapid Communications*, *27*, 1362–1366.
- Hill, C. A. S., Jones, D., Strickland, G., & Centin, N. S. (1998). Kinetic and mechanistic aspects of the acetylation of wood with acetic anhydride. *Holzforschung*, *52*, 623–629.
- Hu, W., Chen, S., Li, X., Shi, S., Shen, W., Zhang, X., et al. (2009). In situ synthesis of silver chloride nanoparticles into bacterial cellulose membranes. *Materials Science and Engineering C*, *29*, 1216–1219.
- Ifuku, S., Nogi, M., Abe, K., Handa, K., Nakatsubo, F., & Yano, H. (2007). Surface modification of bacterial cellulose nanofibers for property enhancement of optically transparent composites: Dependence on acetyl-group DS. *Biomacromolecules*, *8*, 1973–1978.
- Iguchi, M., Yamanaka, S., & Budhiono, A. (2000). Bacterial cellulose—a masterpiece of nature arts. *Journal of Materials Science*, *35*, 261–270.
- John, M. J., & Anandjiwala, R. D. (2008). Recent developments in chemical modification and characterization of natural fiber-reinforced composites. *Polymer Composites*, *29*, 187–207.
- John, M. J., Franci, B., Varughese, K. T., & Thomas, S. (2008). Effect of chemical modification on properties of hybrid fiber biocomposites. *Composites Part A – Applied Science and Manufacturing*, *39*, 352–363.
- Li, J., Zhang, L. P., Peng, F., Bian, J., Yuan, T.-Q., Xu, F., et al. (2009). Microwave-assisted solvent-free acetylation of cellulose with acetic anhydride in the presence of iodine as a catalyst. *Molecules*, *14*, 3551–3566.
- Li, X., Chen, S., Hu, W., Shi, S., Shen, W., Zhang, X., et al. (2009). In situ synthesis of CdS nanoparticles on bacterial cellulose nanofibers. *Carbohydrate Polymers*, *76*, 509–512.
- Maneering, T., Tokura, S., & Rujiravanit, R. (2008). Impregnation of silver nanoparticles into bacterial cellulose for antimicrobial wound dressing. *Carbohydrate Polymers*, *72*, 43–51.
- Nishino, T., Matsuda, I., & Hirao, K. (2004). All cellulose composite. *Macromolecules*, *37*, 7683–7683.
- Nogi, M., Abe, K., Handa, K., Nakatsubo, F., Ifuku, S., & Yano, H. (2006). Property enhancement of optically transparent bionanofiber composites by acetylation. *Applied Physics Letters*, *89*, 233123.
- Nogi, M., Ifuku, S., Abe, K., Handa, K., Nakagaito, A. N., & Yano, H. (2006). Fiber-content dependency of the optical transparency and thermal expansion of bacterial nanofiber reinforced composites. *Applied Physics Letters*, *88*, 133124.
- Page, D. H., & Elhosseiny, F. (1983). The mechanical-properties of single wood pulp fibers. Part VI. Fibril angle and the shape of the stress-strain curve. *Journal of Pulp and Paper Science*, *84*, 99–100.
- Phukan, P. (2004). Iodine as an extremely powerful catalyst for the acetylation of alcohols under solventfree conditions. *Tetrahedron Letters*, *45*, 4785–4787.
- Ren, J. L., Sun, R. C., Liu, C. F., Cao, Z. N., & Luo, W. (2007). Acetylation of wheat straw hemicelluloses in ionic liquid using iodine as a catalyst. *Carbohydrate Polymers*, *70*, 406–414.
- Sakurada, I., Nukushina, Y., & Ito, T. (1962). Experimental determination of elastic modulus of crystalline regions in oriented polymers. *Journal of Polymer Science*, *57*, 651–660.
- Samios, E., Dart, R. K., & Dawkins, J. V. (1997). Preparation, characterization and biodegradation studies on cellulose acetates with varying degrees of substitution. *Polymer*, *38*, 3045–3054.
- Sassi, J.-F., Tekely, P., & Chanzy, H. (2000). Relative susceptibility of the I<sub>α</sub> and I<sub>β</sub> phase of cellulose towards acetylation. *Cellulose*, *7*, 119–132.
- Satgé, C., Verneuil, B., Branland, P., Granet, R., Krausz, P., Rozier, J., et al. (2002). Rapid homogeneous esterification of cellulose induced by microwave irradiation. *Carbohydrate Polymers*, *49*, 373–376.
- Siró, I., & Plackett, D. (2010). Microfibrillated cellulose and new nanocomposite materials: A review. *Cellulose*, *17*, 459–494.
- Vanderhart, D. L., Hyatt, J. A., Atalla, R. H., & Tirumalai, V. C. (1996). Solid-state <sup>13</sup>C NMR and Raman studies of cellulose triacetate: Oligomers, polymorphism, and inference about chain polarity. *Macromolecules*, *29*, 730–739.
- Wu, J., Zhang, J., Zhang, H., He, J., Ren, Q., & Guo, M. (2004). Homogeneous acetylation of cellulose in a new ionic liquid. *Biomacromolecules*, *5*, 266–268.
- Yamamoto, H., Horii, F., & Hirai, A. (2006). Structural studies of bacterial cellulose through the solid-phase nitration and acetylation by CP/MAS <sup>13</sup>C NMR spectroscopy. *Cellulose*, *13*, 327–342.
- Yang, Z., Xu, S., Ma, X., & Wang, S. (2008). Characterization and acetylation behavior of bamboo pulp. *Wood Science and Technology*, *42*, 621–632.
- Yano, H., Sugiyama, J., Nakagaito, A. N., Nogi, M., Matsuura, T., Hikita, M., et al. (2005). Optically transparent composites reinforced with networks of bacterial nanofibers. *Advanced Materials*, *17*, 153–155.