# Synthesis and Characterization of Alkylated Bacterial Cellulose in an Ionic Liquid

Jinmin Qin, Zhiyu Qin, Xueqiong Yin,* Qinhuan Zeng, and Li Zhu

Bacterial cellulose was alkylated by alkyl halide in the ionic liquid 1-butyl-3-methylimmidazolium chloride ([Bmim]Cl) with NaH as the alkaline agent. The derivatives were characterized using Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, elemental analyses, X-ray diffraction, and thermal gravimetric analyses. The resultant bacterial cellulose alkylated derivatives (BCADs) had a degree of substitution (DS) between 0.21 and 2.01. The effects of the alkylating agent, reactant amount, and temperature on the DS were investigated. BCADs with a butyl substituent had a higher DS than did those with ethyl or propyl groups. The crystallinity and thermal stability of the derivatives decreased after modification owing to the change in morphological structure.

*Keywords: Bacterial cellulose; Alkylation; Characterization; Ionic liquid*

*Contact information: Hainan Provincial Fine Chemical Engineering Research Center, Hainan University, Haikou, Hainan, 570228, P.R. China; * Corresponding author: yxq88@hotmail.com*

## INTRODUCTION

Bacterial cellulose (BC) is a kind of cellulose synthesized by bacteria (such as *Acetobacter, Sarcina,* and *Agrobacterium* sp.), fungi, and also algae (Lin *et al*. 2013; Qin *et al.* 2014). BC is different from plant cellulose (PC) in that it is more chemically pure (> 98%), has a higher degree of polymerization (DP, ~10,000), is mechanically stronger (with Young's modulus 15 to 35 GPa, tensile strength 200 to 300 MPa), and has thinner microfibrils (50 to 80 nm, about 200 times thinner than cotton) than PC (Huang *et al.* 2014). Due to its unique structure and properties, BC has drawn increasing interest from many fields, such as biomaterials, the food and paper industries, environmental science, sensors, electronics, *etc.* (Keshk 2014; Chen *et al.* 2014).

Owing to its high molecular weight, high crystallinity, and strong hydrogen network, BC has poor solubility, which limits its potential applications. Having only hydroxyl groups on its polymer framework results in limited functionalities of BC. In order to enhance its properties (adsorption, biodegradability, biomedical, conductivity, catalysis, amphiphillic, solubility, *etc.*), BC was chemically modified to prepare BC derivatives through such methods as carboxymethylation (Tabuchi *et al.* 1998), sulfation (Qin *et al.* 2014), acetylation (Sun *et al.* 2007), phosphorylation (Fox and Edgar 2011), benzoylation (Kamitakahara *et al*. 2009), succinylation (Roy *et al.* 2009), silylation (Tabuchi *et al.* 1998), carbanilation (Czaja *et al*. 2004), and oxidation (Chen *et al.* 2014), *etc*. Chemical modifications of BC have been carried out both heterogeneously and homogeneously. Generally, homogeneous reactions are more efficient than heterogeneous reactions.

In recent years, the homogeneous modification of cellulose in ionic liquids has attracted more attention. Ionic liquids are a group of low-melting salts containing a bulky

cation (imidazolium, phosphonium, pyridinium, ammonium, *etc*.) and an anion (chloride, bromide, acetate, formate, $BF_4^-$ , $PF_6^-$ , $OH^-$, *etc*.), which can exist as liquids at relatively low temperatures (<100 °C). Owing to its non-volatility, non-flammability, good solvating ability, and recyclability, an ionic liquid is considered to be a "green" cellulose solvent (Heinze *et al*. 2008). It was found that certain ionic liquids could dissolve cellulose better than common cellulose solvents. For example, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) could dissolve cellulose very easily without derivatization and degradation, and the content of cellulose could reach 18 to 25 wt%. Many homogeneous modifications of cellulose have been carried out efficiently in ionic liquids. Reports of BC modification in ionic liquid were limited until recently. Schlufter *et al.* (2006) reported successful homogeneous acetylation and carbanilation of BC in ionic liquid. Compared to cellulose from plants (and significantly lower DP) a higher degree of substitution (DS) was obtained for acetylation while a lower reactivity was found for carbanilation.

Though there has been some progress on BC modification, existing knowledge is far from what is required to develop applications for it. Therefore, it is necessary to establish more BC modification procedures to explore wider applications, especially regarding environmental and economic issues. Alkyl cellulose is a kind of cellulose derivative widely used as an additive in architecture, foods, pharmaceuticals, cosmetics, paint, oil recovery, *etc*. This study was aimed at the preparation of bacterial cellulose alkylated derivatives (BCADs) in ionic liquid. The effects of reactant amount, alkylation agent, and temperature on the DS and solubility were evaluated. BCADs were characterized using Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), X-ray diffraction (XRD), elemental analyses (EA), and thermal gravimetric analyses (TG).

## EXPERIMENTAL

### Material

BC was prepared according to the procedure in our previous report (Qin *et al.* 2014). First, the cultured substances on the surface of BC gels were removed by washing with running tap water. Secondly, the gels were stirred in 1% (w/V) NaOH solution for 24 h at 70 °C, followed by washing with distilled water until the filtrate became neutral. Then, the gels were submerged into ethanol for 12 h to remove organic impurities. Finally, the BC gels were washed with distilled water and vacuum dried at 80 °C to obtain the purified BC. The dried BC materials were crushed into 40 mesh powder and dried under a vacuum for 6 h at 120 °C for future modification. [Bmim]Cl was purchased from Sigma–Aldrich and dried under vacuum at 120 °C over phosphorus pentoxide before use. N,N-dimethyl formamide (DMF) was dried by zeolite for 5 h and vacuum distillation at 125 °C to 135 °C.

### Preparation of Bacterial Cellulose Alkylated Derivatives (BCADs)

0.5 g of BC and 10 g of ionic liquids were added into a three-neck flask. The mixture was heated at 100 °C and stirred for 24 h under the protection of nitrogen. When BC was completely dissolved, the temperature was reduced to 60 °C, followed by the addition of 5 mL DMF into the solution. Then, 2.2248 g NaH was added to the solution and reacted at 60 °C for 30 min. Subsequently, 6.9 mL ethyl bromide was added and stirred

for 6 h under reflux. Finally, the product was precipitated in methanol and washed three times with methanol and obtained after vacuum drying at 60 °C.

### Characterization of BCADs

The FTIR spectra were measured on a Bruker TENSOR27 spectrometer, with the samples immobilized in KBr and scanned in the range of 4000 to 450 $cm^{-1}$. The $^{13}C$ NMR spectra of the BCADs were recorded on a Bruker AV 400 NMR spectrometer at 27 °C in deuterated dimethyl sulfoxide (DMSO), with tetramethyl silane (TMS) as the internal standard. XRD diagrams were recorded with a Bruker-AXS D8 high resolution X-Ray powder diffractometer in reflection mode with following conditions: Cu target, Ni filter, 40 kv tube voltage, 40 mA tube current, and scanning range of 5° to 40°. Thermo-gravimetric analysis was measured on a SDT Q600 Thermo Gravimetric Analyser under the following conditions: $N_2$ atmosphere, heating rate of 10 °C/min, and temperature range of 30 to 700 °C. The EA results were obtained with a VarioMicro cube elemental analyzer. The DS values were calculated according to Eq. 1:

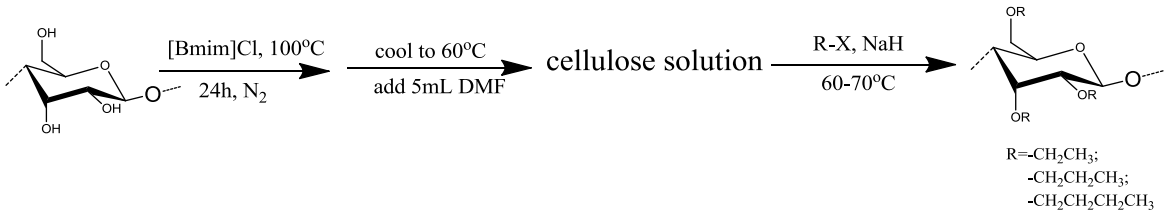
$$DS = \frac{18C\% + 162H\% - 18}{n \times (C\% - 27H\% + 3)} \quad (1)$$

where DS is the degree of substitution, *n* is the carbon number of the alkyl, C% is the carbon content of the BCADs, and H% is the hydrogen content of the BCADs.

## RESULTS AND DISCUSSION

### Preparation and Solubility of BCADs

BC was modified with different kinds of alkyl halide (RX) in ionic liquid [Bmim]Cl, where NaH was used as the alkaline agent to bind the acid released (shown in scheme 1). To ensure a complete binding of the acid, the molar ratio of NaH and alkyl reagent was adopted to be 1:1.




**Scheme 1.** Reaction scheme of BC alkylation in ionic liquid [Bmim]Cl

Alkylation of cellulose usually requires a long time for the reaction, even up to a few days depending on the alkylation agent (Wang 2013). Most reactions in ionic liquid are faster than in normal solvents (Elschner *et al*. 2014). Therefore, all the reactions here were carried out for 6 h. The DS values were calculated according to the elemental analysis results. The alkylation of BC in [Bmim]Cl with NaOH as the base was also investigated. However, the solution became red immediately after NaOH was added. The reaction was not successful, and there was no FTIR signal indicating an alkyl group in the product. Both alkylation and ionic liquid are sensitive to water. The failure of reaction with NaOH might

be due to an increased amount of water generated from deprotonation of imidazolium. Therefore, NaH was used in present procedure. The effects of different alkyl halide types (ethyl bromide, ethyl iodide, 1-propyl bromide, 1-butyl bromide), molar ratios of the reactants (n(AGU):n(NaH):n(RX) in ratios of 1:9:9, 1:12:12, 1:15:15, and 1:30:30), and different reaction temperatures (60 °C, 70 °C) on the DS and solubility were investigated. The results were listed in Table 1.

**Table 1.** Preparation Conditions and Solubility of Alkylated Bacterial Cellulose

| Samples | Name | Alkyl Halide | Molar Ratio of The Reactants | | | Solubility[a] | |
|---|---|---|---|---|---|---|---|
| | | | n(AGU):n(NaH):n(RX)[b] | *T* (°C) | DS | DMSO | 6 wt% NaOH |
| 1 | ECA1 | $CH_3CH_2Br$ | 1:12:12 | 60 | 0.21 | O | O |
| 2 | ECA2 | $CH_3CH_2Br$ | 1:15:15 | 60 | 0.31 | O | + |
| 3 | ECA3 | $CH_3CH_2Br$ | 1:30:30 | 60 | 0.69 | + | + |
| 4 | ECA4 | $CH_3CH_2I$ | 1:30:30 | 60 | 1.41 | + | + |
| 5 | ECA5 | $CH_3CH_2I$ | 1:30:30 | 70 | 1.73 | + | + |
| 6 | PCA1 | 1-$CH_3CH_2CH_2Br$ | 1:30:30 | 60 | 0.48 | + | - |
| 7 | BCA1 | 1-$CH_3CH_2CH_2CH_2Br$ | 1:30:30 | 60 | 1.44 | + | - |
| 8 | BCA2 | 1-$CH_3CH_2CH_2CH_2Br$ | 1:30:30 | 70 | 2.01 | + | - |

[a] Solubility in DMSO and 6% (w/v) NaOH： + soluble; O Swelling; - insoluble.
[b] AGU: anhydroglucose unit of the cellulose

As shown in Table 1, under the same conditions (60 °C, 6 h), the DS of the samples modified by ethyl bromide (ECA1-ECA3) changed from 0.21 to 0.69 with an increase in the molar ratio of the reactants. The DS could not reach a high number, even though excess ethyl bromide was put into the system. The actual amount of ethyl bromide in solution was less than the imported amount and uncertain owing to the boiling point of ethyl bromide (38.4 °C) being lower than the reaction temperature (60 °C). Compared to ethyl bromide, ethyl iodine is more reactive. ECA4 yielded a much higher DS than ECA3 obtained under the same conditions because of the higher reactivity of ethyl iodine. With the increase in reaction temperature, the DS increased in both systems with ethyl iodine and butyl bromide.

Compared to BC alkylation in DMAc/LiCl with similar amount NaH and ethyl bromide (BC: NaH: ethyl bromide (molar ratio): 1: 28: 20) at 50 °C for 110 h (Lin *et al.* 2013), the DS of the products was not highly efficient as acylation in [BmimCl] (Barthel and Heinze 2006). Ionic liquid is a good solvent for cellulose. However, ionic liquid [BmimCl] could deprotonate at C-2 and reacts with the reducing ends of cellulose (Sowmiah *et al*. 2009). Bases, such as impurities in IL or additional added base, catalyze the side reaction, which could happen in 2 h and increase with the reaction time (Ebner *et al*. 2008). NaH is a very strong base. There would be competitive reactions between deprotonation of imidazolium nucleus and deprotonation of hydroxyl group, with the assistance of NaH; competitive reactions between deprotonated imidazolium nucleus and cellulose hydroxyl group with alkyl halide. Those might be the reasons that more NaH and alkyl halide were required in the alkylation procedure. The deprotonation at C-2 is the key

step for the side reaction. Therefore, a 2-substituted ionic liquid could be considered for future modification of cellulose under basic conditions to avoid the side reaction.

Another interesting result should be mentioned—the DS did not change regularly with the increase in alkyl length. Propyl bromide had the lowest DS among ethyl bromide, propyl bromide, and butyl bromide, while butyl bromide had the highest. The results were different from the alkylation in DMAc/LiCl, where the longer the alkyl group, the lower the DS was, resulting from the effects of electrophilicity and steric hindrance of the alkyl groups (Lin *et al.* 2013). Ionic liquids can exhibit unique relationships for cellulose dissolution; Erdmenger *et al*. (2007) found a strong odd-even effect for the dissolution of cellulose in ionic liquid with small alkyl chains (below six carbon units). Cellulose was more soluble in 1-alkyl-3-methylimidazolium-based ionic liquids with even-numbered alkyl chains than in those with odd-numbered alkyl chains. Cellulose had the best solubility in [$C_4$mim]Cl and the lowest in [$C_3$mim]Cl. Ethyl bromide had the best reactivity in the present work; this might have resulted from it having the same alkyl group as the solvent, which enabled the alkyl agent to be more compatible with cellulose/ionic liquid solution. However, Heinze *et al.* (2008) reported that in the homogeneous acylation of cellulose in [$C_4$mim]Cl, the products prepared from acid anhydride contained similar lengths of alkyl chains, as the alkyl chain of the ionic liquid's cation had a low degree of acylation. The relation between the two alkyl chain lengths of the acid anhydride and ionic liquid was not certain. All the results expressed that cellulose in ionic liquid had an optimal chain length for dissolution and modification, but the reasons for this were not clear and should be investigated further in the future.

As listed in Table 1, ECA had good solubility in DMSO and 6 wt% NaOH solution. ECA with a DS higher than 0.26 could dissolve both in DMSO and 6 wt% NaOH. However, PCA and BCA could only dissolve in DMSO, not in 6% NaOH solution, which might result from the hydrophobicity of the longer alkyl groups.

## Characterization of BCADs

Figure 1 illustrates the FTIR spectra of some BCADs (BCA 2(a, DS 2.01), PCA1(b, DS 0.48), ICA1(c, DS 1.41), ECA4(d, DS 0.69), and BC(e)).

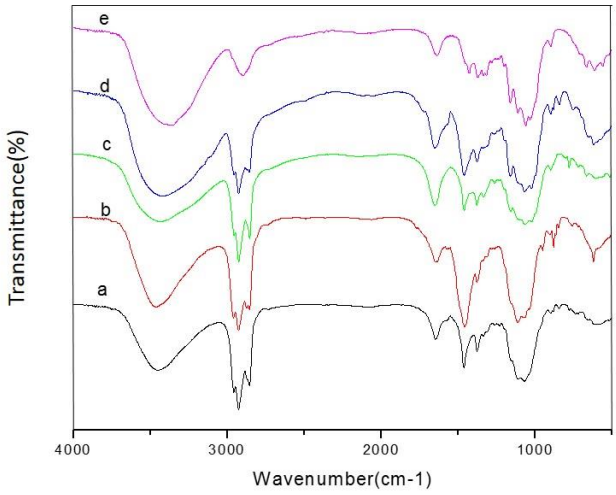



**Fig. 1.** FTIR spectra of BCA 2(a, DS 2.01), PCA1(b, DS 0.48), ECA4(c, DS 1.41), ECA3(d, DS 0.69) and BC(e)

On the BC spectrum, the broad peak at 3420 $cm^{-1}$ corresponded to the O-H stretching vibration, which indicated that BC contained a large number of highly associative and strong hydrogen bonds. The peaks at 2910 $cm^{-1}$ and at 1337 $cm^{-1}$ were assigned to the C-H stretching and C-H bending vibrations, respectively. The peaks at 1163 $cm^{-1}$ and 1060 $cm^{-1}$ corresponded to C-H and C-O-H stretches on the pyranose ring. All these peaks were characteristic of BC (Sun *et al*. 2007). For the BACDs, the peak at 3420 $cm^{-1}$ was upshifted and weakened, which illustrated that some of the hydrogen bonds had been broken, and the hydroxyl groups in BC were partially replaced by alkyl moiety. Markedly increased strength of the peaks at 2925 $cm^{-1}$ corresponded to $-CH_2-$ and $-CH_3$ stretches (Fox and Edgar 2011). The change in the FTIR spectra verified that alkylation had been successfully carried out to BC.

Figure 2 shows the $^{13}$C-NMR spectrum of the ethyl bacterial cellulose (ECA5, DS1.73) in DMSO-$d_6$ at room temperature. The methyl group and methylene group of the ethoxy ($-OCH_2CH_3$) function were located at 15.6 ppm and 66.2 ppm, respectively (Kamitakahara *et al*. 2009). The signal at 103.2 ppm was due to C-1, and the one at 75.3 ppm was assigned to C-4. The signal for C6 appeared at 60.7 ppm, indicating that C6 had been completely ethylated and the reactivity of the OH was higher at the C6 position than at the other positions. The signals of substituted C2 and C3 appeared at 80.7 ppm (Kondo and Gray 1991). Unmodified C2, C3, and C5 showed up at 75.3 ppm. The NMR spectrum further confirmed the presence of an ethyl group.

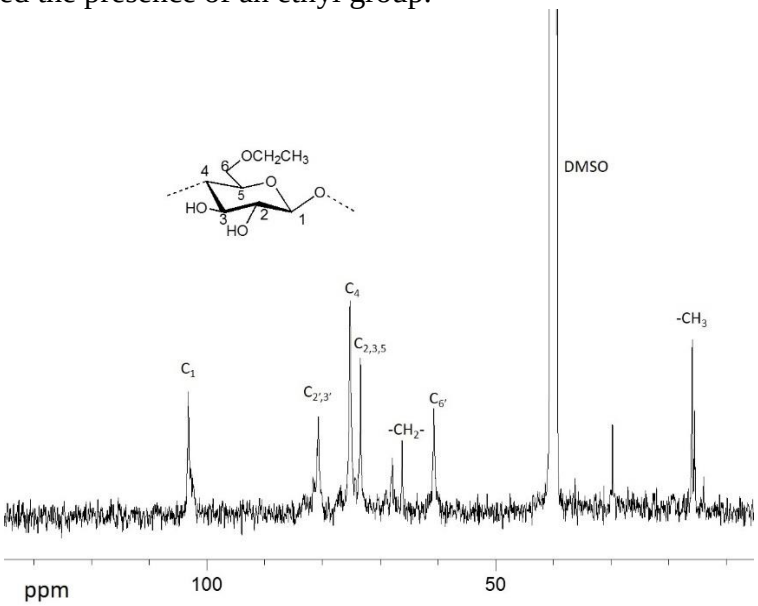



**Fig. 2.** $^{13}$C-NMR spectra of the ethyl bacterial cellulose (ICA2)

The XRD patterns of BC (a) and the BC derivatives (ECA5 (b, DS 1.73), PCA1 (c, DS0.48) and BCA1 (d, 2.01)) are shown in Fig. 3. In the XRD pattern of BC, the angles of three diffraction peaks ($2\theta$) are 14.6°, 16.7°, and 22.7° corresponded to the characteristic diffraction peaks of cellulose in the crystal plane of ($1\bar{1}0$), (110) and (200), respectively. This indicated that BC had a cellulose I crystalline structure (Czaja *et al*. 2004). In the XRD pattern of ECA5, the three characteristic diffraction peaks disappeared, and a strong broad peak at 20.2° appeared after alkylation. The results revealed that the original straight parallel chain structure of cellulose had been destroyed during dissolution and subsequent homogeneous modification in ionic liquid, and ECA5 had an obvious amorphous structure.

The patterns of PCA1 (c) and BCA1 (d) in Fig. 3 had new diffraction peaks, which indicated that some ordered structure in the two derivatives had formed after modification and precipitation.

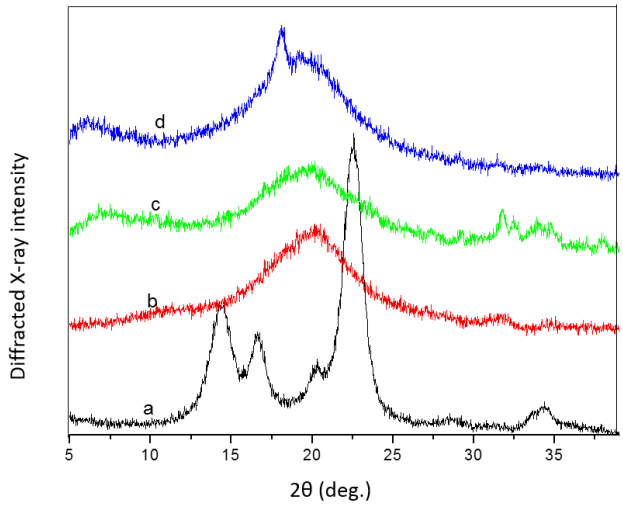



**Fig. 3.** X-ray diffraction patterns of BC (a) and ECA5 (b), PCA1 (c), and BCA1 (d)

The thermal stabilities of the BCADs and BC were measured using TGA. The TGA thermograms for BC and BCADS are shown in Fig. 4, and the thermal decomposition data are listed in Table 2. As shown in Fig 4, the amount of weight lost increased with the increase in temperature. For BC, the weight lost below 300 °C was due to dehydration and the structural cleavage of the polymer. The continuous weight loss around 350 °C was due to the degradation of the remaining residue. As listed in Table 2, the decomposition temperatures (T1, T2) of the BCADs were lower than those of BC raw material, indicating that the thermal stability of BCADs were lower than that of BC. ECA3 had better thermal stability than ECA5, which might have been due to lower DS keeping a more ordered structure of ECA5. The XRD pattern showed that PCA1 and BCA1 had a more ordered structure than ECA5. Therefore, PCA1 and BCA1 had better thermal stability than ECA. The results expressed that the differences of thermal stability mainly resulted from the changes in crystallinity and morphology structure which were affected by the alkyl group and the degree of substitution.

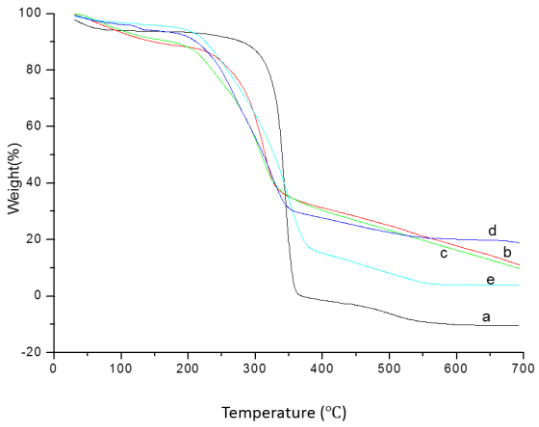



**Fig. 4.** The TGA results of BC(a), ECA3(b), ECA5(c), PCA1(d) and BCA1(e)

**Table 2.** Decomposition Temperatures of the BC and BCADs

| Samples | Alkyl halide | DS | Decomposition Temperatures (°C) | | Maximum Weight loss (%) |
|---|---|---|---|---|---|
| | | | T1 | T2 | |
| BC | | - | 296.5 | 343.38 | 95.41 |
| ECA3 | $CH_3CH_2Br$ | 0.69 | 201.5 | 312.48 | 58.32 |
| ECA5 | $CH_3CH_2I$ | 1.73 | 181.5 | 308.94 | 60.66 |
| PCA1 | 1- $CH_3CH_2CH_2Br$ | 0.48 | 204.5 | 326.6 | 66.39 |
| BCA1 | 1- $CH_3CH_2CH_2CH_2Br$ | 2.01 | 225.5 | 349.56 | 81.68 |

## CONCLUSIONS

1. Bacterial cellulose alkylated derivatives with DS ranging from 0.21 to 2.01 were successfully prepared through direct homogeneous alkylation of BC with alkyl halide in ionic liquid 1-butyl-3-methylimidazolium chloride. The results indicated that the alkyl length affected the reaction in addition to the reactant amount and temperature.
2. Alkyl bacterial cellulose with butyl had the highest degree of substitution among ethyl, propyl, and butyl cellulose. Research into the influences of alkyl length should be investigated further.
3. The reaction was carried out for 6 h to investigate other parameters. The influence of the reaction's duration should also be optimized to decrease the usage of the alkylation agent.
4. Bacterial cellulose alkylated derivatives have hydrophobic and hydrophilic groups on their backbones, which have the potential to prepare materials with special surface structures or to be used as additives in cosmetics, food, pharmaceuticals, and other fields.

## ACKNOWLEDGMENTS

The authors acknowledge the National Science Foundation of China (Project No. 21264007, 21466011) and the Young Researcher Project of Hainan University (QNJJ1221) for their financial support.

## REFERENCES CITED

Barthel, S., and Heinze, T. (2006). "Acylation and carbanilation of cellulose in ionic liquids," *Green Chem.* 8, 301–306. DOI: 10.1039/b513139a

Chen, S., Yang, J., Li, Z., Wang, H., and Hu, W. (2014). "Functionalized bacterial cellulose derivatives and nanocomposites," *Carbohydr. Polym.* 101, 1043-1060. DOI:10.1016/j.carbpol.2013.09.102

Czaja, W., Romanovicz, D., and Malcolm, B. R. (2004). "Structural investigations of microbial cellulose produced in stationary and agitated culture," *Cellulose* 11(3-4), 403-411. DOI: 10.1023/B:CELL.0000046412.11983.61

Ebner, G., Schiehser, S., Potthast, A., and Rosenau, T. (2008). "Side reaction of cellulose with common 1-alkyl-3-methylimidazolium-based ionic liquids," *Tetrahedron Lett.* 49, 7322-7324. DOI:10.1016/j.tetlet.2008.10.052

Elschner, T., Koetteritzsch, M., and Heinze, T. (2014). "Synthesis of cellulose tricarbonates in 1-butyl-3-methylimidazolium chloride/pyridine," *Macromol. Biosci* 14, 161165. DOI: 10.1002/mabi.201300345

Erdmenger, T., Haensch, C., Hoogenboom, R., and Schubert, U. S. (2007). "Homogeneous Tritylation of Cellulose in 1-Butyl-3-methylimidazolium Chloride," *Macromol. Biosci* 7, 440-445. DOI: 10.1002/mabi.200600253

Fox, S. C., and Edgar, K. J. (2011). "Synthesis of regioselectively brominated cellulose esters and 6-cyano-6-deoxycellulose esters," *Cellulose* 18(5), 1305-1314. DOI: 10.1007/s10570-011-9574-3

Heinze, T., Dorn, S., Schoebitz, M., Liebert, T., Koehler, S., and Meister, F. (2008). "Interactions of ionic liquids with polysaccharides–2: Cellulose," *Macromol. Symp* 262, 8-22. DOI: 10.1002/masy.200850202

Huang, Y., Zhu, C., Yang, J., Nie, Y., Chen, C., and Sun, D. (2014). "Recent advances in bacterial cellulose," *Cellulose* 21, 1-30. DOI: 10.1007/s10570-013-0088-z

Kamitakahara, H., Funakoshi, T., Takano, T., and Nakatsubo, F. (2009). "Syntheses of 2, 6-O-alkyl celluloses: Influence of methyl and ethyl groups regioselectively introduced at O-2 and positions on their solubility," *Cellulose* 16(6), 1167-1178. DOI: 10.1007/s10570-009-9332-y

Keshk, S. M. (2014). "Bacterial cellulose production and its industrial applications," *J. Bioproc. Biotechniq.* 4, 150-159 (DOI: 10.4172/2155-9821.1000150)

Kondo, T., and Gray, D. G. (1991). "The preparation of O-methyl- and O-ethyl-celluloses having controlled distribution of substituents," *Carbohydr. Res.* 220,173-183. DOI: 10.1016/0008-6215(91)80015-F

Lin, S.-P., Calvar, I. L., Catchmark, J. M., Liu, J.-R., Demirci, A., and Cheng, K.-C. (2013). "Biosynthesis, production and applications of bacterial cellulose," *Cellulose* 20, 2191-2219 DOI 10.1007/s10570-013-9994-3

Lin, Y., Yu, C., Zhu, L., Yin, X., Lao, B., and Lin, Q. (2013). "Synthesis and characterization of alkyl bacterial cellulose through etherification with alkyl bromide in DMAc/LiCl," *Appl. Mech. Mater.* 320, 478-482. DOI: 10.4028/www.scientific.net/AMM.320.478

Qin, Z., Ji, L., Yin, X., Zhu, L., Lin, Q., and Qin, J. (2014). "Synthesis and characterization of bacterial cellulose sulfates using a $SO_3$/pyridine complex in DMAc/LiCl," *Carbohydr. Polym* 101, 947- 953.

Roy, D., Semsarilar, M., Guthrie, J. T., and Perrier, S. (2009). "Cellulose modification by polymer grafting: A review," *Chem. Soc. Rev.* 38(7), 2046-2064. DOI: 10.1039/B808639G

Schlufter, K., Schmauder, H.-P., Dorn, S., and Heinze, T. (2006). "Efficient homogeneous chemical modification of bacterial cellulose in the ionic liquid 1-N-

butyl-3-methylimidazolium chloride," *Macromol. Rapid Comm.* 27, 1670-1676. DOI: 10.1002/marc.200600463

Sowmiah, S., Srinivasadesikan V., Tseng M.-C., and Chu Y.-H. (2009). "On the chemical stabilities of ionic liquids," *Molecules* 14, 3780-3813. DOI: 10.3390 /molecules 14093780)

Sun, D., Zhou, L., Wu, Q., and Yang, S. (2007). "Preliminary research on structure and properties of nanocellulose," *J. Wuhan University Technology: Materials Sci. Edition* 22 (4), 677-680. DOI: 10.1007/s11595-006-4677-7

Tabuchi, M., Watanabe, K., and Morinaga, Y. (1998). "Acetylation of bacterial cellulose: preparation of cellulose acetate having a high degree of polymerization," *Biosci. Biotech. Bioch.* 62(7), 1451-1454. DOI:10.1271/bbb.62.1451

Wang, Y. (2013). "Synthesis and characterization of regioselective cellulose derivatives," Dissertation. Friedrich-Schiller- Universität Jena.

Article submitted: November 3, 2014; Peer review completed: January 11, 2015; Revised version received and accepted: February 6, 2015; Published: February 16, 2015.