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ORIGINAL PAPER

Comparison of succinylation methods for bacterial cellulose and adsorption capacities of bacterial cellulose derivatives for Cu^{2+} ion

Xueqiong Yin · Changjiang Yu · Xiaoli Zhang · Jianxin Yang · Qiang Lin · Jinbang Wang · Qingmei Zhu

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Abstract Bacterial cellulose (BC) was homogenously modified with succinic anhydride in *N*,*N*-dimethylacetamide/LiCl in the presence of triethylamine and heterogeneously in pyridine in the presence of 4-dimethylaminopyridine. FTIR, XRD, 13C CP MAS NMR, SEM were used to characterize BC and succinylated bacterial cellulose (SBC). For homogeneous modification, the degree of substitution (DS) of SBC differs from 0.21 to 1.45 with the variation of the adding amount of succinic anhydrate, temperature, reaction time, and the amount of triethylamine. DS and XRD profiles reveal that heterogenous reaction mainly happens on the surface of BC membrane. The adsorption capacity and mechanism of Cu^{2+} onto BC and SBC were investigated. The result shows the adsorption is affected by the morphology and the DS of adsorbents.

Keywords Bacterial cellulose · Succinic anhydride · Modification · Characterization · Cu^{2+} adsorption

Introduction

Cellulose is the most abundant biopolymer on earth. Cellulose and its derivatives have been widely used in fundamental research and industry. Bacterial cellulose (BC), an exocellular polysaccharide of bacteria belonging to the genera *Acetobacter*, *Rhizobium*, *Agrobacterium*, and *Sarcina*, is the same unbranched polymer of β-1,4-linked glucopyranose residues as plant cellulose (PC). However, the supramolecular

X. Yin (✉) · C. Yu · J. Yang · Q. Lin · J. Wang · Q. Zhu
Key Laboratory of Application Technology of Hainan Superior Resources Chemical Materials, Ministry of Education of China, Hainan Universtiy, 570228 Haikou, Hainan Province, China
e-mail: yxq88@hotmail.com

X. Zhang
Northwest Research Institute of Chemical Industry, 710600 Lintong, Shan'Xi Province, China

structure and physiochemical properties of BC differ from those of PC. Comparing with PC, BC usually has higher degree of polymerization (DP, 2000–6000), higher chemical purity (>98%), and smaller ultrafine reticulated fiber structure (3 ± 4 (thickness) × 70 ± 80 nm (width),) higher Young's modulus, and higher water-adsorption capacity, which enable wide applications of BC [1].

Chemical derivatization of BC is not as widely researched as that of PC, while it has been paid more and more attention in recent years. BC expresses different chemical behaviors from PC. Geyer et al. [2] executed carboxymethylation, silylation, and acetylation on BC. Under comparable synthesis conditions, carboxymethylated cellulose (CMC) starting from BC has higher amounts of mono- and di-*O*-carboxymethyl residues, lower amounts of tri-*O*-carboxymethylated residue and unsubstituted units than CMC from PC. Schlufter et al. [3] modified BC (DP 6500) in ionic liquid 1-*N*-butyl-3-methylimidazolium chloride, getting well-soluble BC acetates and carbanilates under homogeneous and mild reaction conditions. Distribution of the acetyl moieties is in the order of O-6 > O-3 > O-2 (PC prefers O-6 > O-2 > O-3 [4]).

Modification of BC is a good way to understand more about the special biopolymer and get more valuable products from BC. Comparing with BC, BC derivatives express improved properties. Oshima et al. [5] modified BC with phosphoric acid in DMF along with urea. Phosphorylate of BC exhibits selective adsorption behaviors for various transition metal ions and lanthanide ions. Wang et al. [6] synthesized benzoylated bacterial cellulose (BBC) from benzoyl chloride and BC. BBC displays thermotropic liquid crystalline feature. Ifuku et al. [7] surface acetylated BC to enhance the properties of optically transparent composites of acrylic resin reinforced with the BC. It was found acetylation of BC changes the surface properties of the composite and reduces the moisture content of the composite to about one-third of untreated composite. Furthermore, acetylation reduces the coefficient of thermal expansion of BC sheet from 3×10^{-6} to below 1×10^{-6} K^{-1}.

Cellulose derivatives containing carboxyl group are widely used in food, paper, cosmetic, environment, and medicine industries [8]. Succinic anhydride is a potential agent to modify cellulose via acylation to get derivatives with carboxyl group. In this paper, homogenous modifications of BC with succinic anhydride in the presence of triethylamine in DMAc/LiCl and heterogeneous modifications in the presence of DMAP in pyridine were investigated, respectively. Adsorption capacities for Cu^{2+} of BC and the modified BC were also studied.

Experimental

Materials

Bacterial cellulose (BC), being 1 cm × 1 cm × 0.2 cm small pieces, prepared by incubation of *Acetobacter* in a culture media containing coconut water, was supplied by Haikou Meilanqiao Nata Factory. BC gel was washed under running tap water for 24 h to remove the cultural substances on the surface. And then BC was

immersed and stirred in 1% (w/V) NaOH solution at 70 °C for 24 h. After washed with distilled water until the filtrate became neutral, BC was separated to two parts. One part was dried under vacuum at 80 °C for 20 h. Another part was lyophilizated. Lithium chloride (LiCl) was dried at 150 °C for 12 h over potassium hydroxide under vacuum [9]. Succinic anhydride was purchased from Sinopharm Chemical Reagent Co., Ltd and used as received.

Homogenous succinylation of BC

1.0 g of BC (6.3 mmol) was suspended in 40 mL of *N*,*N*-dimethylacetamide (DMAc) and stirred at 140 °C for 2 h. After the slurry was allowed to cool down to 100 °C, 4.5 g of anhydrous LiCl was added. The cellulose was completely dissolved during cooling to room temperature with constant stirring. The typical procedure of succinylation was performed as follows: triethylamine (3:1 mol/mol anhydroglucose unit (AGU)) in 5 mL of DMAc was added into BC solution, followed by adding succinic anhydrate (3:1 mol/mol AGU) in 5 mL of DMAc. Succinylation was allowed for 30 min at 30 °C with mechanical stirring under the protection of nitrogen. When the reaction ended, succinylated bacterial cellulose (SBC) was precipitated in 300 mL of ethanol and filtrated, washed with ethanol for three times, and then dried at 40 °C under vacuum for 12 h. Light-brown powder product was obtained finally.

Heterogeneous succinylation of BC

After BC was purified according to the above mentioned method, 20 pieces (1 cm × 1 cm × 0.2 cm, the dry weight is about 0.51 g) of wet BC were filtrated to remove water, and then immersed in 20 mL of pyridine for 2 h with stirring. The mixture was filtrated under vacuum. The above procedure was repeated twice to remove the water absorbed inside BC. 4.5025 g (14:1 mol/mol AGU) of succinic anhydrate and 50 mg of dimethylaminopyridine (DMAP) were added to the reactor with the protection of nitrogen. The reaction was allowed for 24 h at 50 °C. When the reaction ended, cellulose derivative was filtrated and washed with distilled water and acetone, and then dried at 60 °C. White-flakes were obtained finally.

Determination of the degree of substitution [10]

0.5 g of SBC was put into a 50 mL Erlenmeyer flask. 20 mL of 0.25 mol/L NaOH standard solution was added, and then continuously stirred for 0.5 h at 50 °C. Two drops of phenolphthalein indicator were added to the flask. The above solution was back-titrated with 0.20 mol/L standard HCl solution until the solution became permanently colorless. The DS was calculated according to Eqs. 1 and 2.

$$n = \frac{c(V_1 - V_2)}{m} \tag{1}$$

$$\mathrm{DS} = \frac{162n}{1000 - 100n} = \frac{0.162n}{1 - 0.100n} \tag{2}$$

where, 162 is the molar mass of AGU (g/mol), 100 is the increased molar mass of substituted AGU (g/mol), N is the consumed acid per gram sample (mmol/g), M is the mass of the sample (g), V_1 is the consumed HCl in blank test (mL), V_2 is the consumed HCl in sample test (mL), C is the concentration of the standard hydrochloride acid, mol/L.

Characterization of SBC

FTIR spectra were measured on a Bruker TENSOR27 spectrometer, using KBr pellet technique. The samples were smashed to smaller than 0.3 mm for X-ray diffraction diagrams measurement. X-ray diffraction diagrams were recorded using a Bruker-AXS D8 Advance X-ray Powder Diffraction System. Nickel-filtered Cu-Ka radiation ($\lambda = 0.15418$ nm) generated at 50 kV and 100 mA was collimated by two pinholes of 0.3 mm diameter. The SEM images were taken on a Hitachi (Japan) S-3000 N SEM. 13C CP MAS NMR spectra were made on a Bruker AV300 Solid NMR Spectrometer with a spinning rate of 4.5 kHz.

Cu^{2+} adsorption test [5]

Six portions of 0.01 g BC were added to 10 mL of 0.25 mg/mL $CuSO_4$ solutions. The mixtures were stirred for different times (10–120 min) at room temperature (28 °C). The mixtures were centrifuged to obtain the supernate. The amount of remaining metal ions in the supernate was determined by an atomic adsorption spectrophotometer (AA-100, Perkin Elemer). The amount of metal ion adsorbed on the adsorbent was calculated according to the Eq. 3

$$\%\text{Adsorption} = \frac{C_0 - C_s}{C_0} \times 100(\%) \tag{3}$$

where C_0 is the initial concentration (mg/mL) of Cu^{2+} ion, C_s is the concentration (mg/mL) of Cu^{2+} ion in the supernate.

Results and discussions

In this study, BC was modified by succinic anhydrate homogenously in DMAc/LiCl in the presence of triethylamine and heterogeneously in pyridine in the presence of DMAP. DS was determined through acid–base titration. The products were characterized with FTIR, XRD, 13C CP MAS NMR, and SEM.

Figure 1 shows the FTIR spectra of unmodified BC and SBC (DS 1.45). In the spectrum of BC, the absorbances at 3408, 2897, 1635, 1370, 1163, and 1060 cm^{-1} are characteristic peaks of cellulose [11]. The peak at 3408 cm^{-1} is due to O–H stretching, and the one at 2897 cm^{-1} is due to CH_2 stretching. The peak at 1635 cm^{-1} is the peak of water absorbed. The peak at 1163 cm^{-1} results from C–O stretching, and that at 1060 cm^{-1} from C–O–C pyranose rings skeletal vibration. The peak at 899 cm^{-1} is the typical absorbance of β-glucosidic linkages between sugar residues. In the spectrum of SBC, new absorbances at 1668, and 1596 cm^{-1}

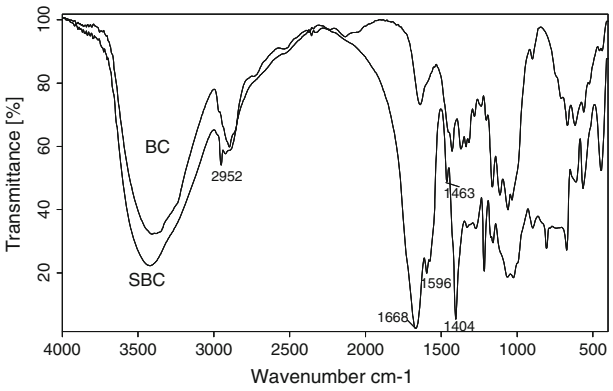

Fig. 1 FTIR spectra of BC and SBC (DS 1.45)

appear. The peak at 1668 cm^{-1} is the overlapped peak of the carbonyl groups in the ester and COOH group [12], and that at 1596 cm^{-1} is from antisymmetric stretching of carboxylic anions [13], which verify the presence of succinyl group. The peaks at 1404, 1463, and 2952 cm^{-1} corresponding to CH_2 scissors vibration, CH_2 symmetric ring stretch at pyranose ring, and CH_2 antisymmetric stretching increased obviously [14] because of the presence of ethylene of the succinyl group.

The CP/MAS 13C NMR spectrum of SBC (DS 1.45) is shown in Fig. 2. There are two peaks at 183 and 181 ppm, which are assigned to –C=O of acetyl and –COOH. The absorbance at 31 ppm derives from the methylene group. The peak around 104 ppm results from C-1. The peaks of C-6 and the substituted C-6 are located at the region around 61 ppm. The other carbons on pyranose ring have absorbances around 83 ppm [15, 16].

Homogenous modification

The effects of succinic anhydrate amount, temperature, reaction time, amount of triethylamine on the DS of SBC were investigated. The plot of molar ratio of succinic anhydrate and BC (1:1, 2:1, 3:1, 4:1, 5:1, 8:1, 10:1) versus DS, reacted in the presence of triethylamine (3:1 mol/mol AGU) at 30 °C for 30 min, was shown in Fig. 3. With the increase of succinic anhydrate amount, DS increased almost linearly when the ratio being less than 5:1. DS reached 0.55 when the ratio was 5:1, and then DS changed slowly with further increase of succinic anhydrate amount. Therefore, 5:1 was chosen for further condition optimizing.

The influences of temperature (Samples 1–5), reaction time (Samples 6–10), and amount of triethylamine (Samples 11–14) on DS were shown in Table 1, with the molar ration of succinic anhydrate and AGU all being 5:1. DS increased with the increase of reaction temperature (15, 20, 30 °C), and reached maximum DS 0.57 at 30 °C. Further increase of temperature resulted in the decrease of DS, DS being 0.39 at 50 °C. Higher temperature is dynamically good for esterification. However,

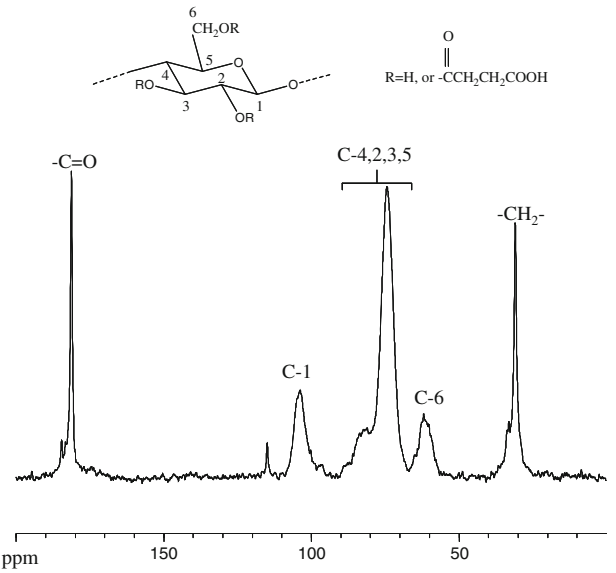

Fig. 2 13C CP MAS NMR spectrum of SBC (DS 1.45)

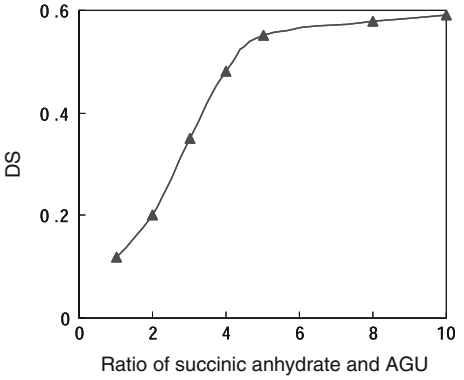

Fig. 3 Effect of succinic anhydrate amount on DS (Reaction taken at 30 °C for 30 min in the presence of triethylamine (3:1 mol/mol AGU))

triethylamine evaporates faster at higher temperature, which dynamically affects the reaction reversely. Therefore, 30 °C is the optimum temperature.

When the reaction time extended from 10 min to 30 min, the DS of product increased obviously from 0.22 to 0.57. Further prolonging of reaction time resulted in slow increase of DS. Triethylamine was used as base to neutralize the byproduct acid. Increasing triethylamine amount resulted in DS increasing. When the molar ratio of triethylamine and AGU was 3:1, the DS reached 0.55. And DS increased to 0.70 when the molar ratio of triethylamine and AGU was 6:1. A reaction lasting for 120 min at 30 °C, with 8:1 of the the molar ratio of triethylamime and AGU, was executed, which resulted in higher DS 1.45 (Sample 15).

Table 1 Succinylated bacterial cellulose prepared at different conditions

Effective factors	Sample	Triethylamine amount (mol:mol AGU)	Reaction time (min)	Temperature (°C)	DS
Temperature	1	3:1	30	15	0.21
	2	3:1	30	20	0.33
	3	3:1	30	30	0.57
	4	3:1	30	40	0.49
	5	3:1	30	50	0.39
Reaction time	6	3:1	10	30	0.22
	7	3:1	15	30	0.45
	8	3:1	20	30	0.50
	9	3:1	30	30	0.57
	10	3:1	50	30	0.64
Amount of triethylamine	11	3:3	20	30	0.24
	12	3:2	20	30	0.42
	13	3:1	20	30	0.55
	14	6:1	20	30	0.70
	15	8:1	120	30	1.45

Table 2 Heterogenous succinylation of bacterial cellulose

Sample	Number of wet BC particles	Dry raw BC (g)	DMAP (mg/mL)	SA:AGU (mol/mol)	Py (mL)	Yield (g)	DS
16	100	2.574	50	4:1	20	2.608	0.12
17	20	0.514	40	14:1	20	0.545	0.16

Heterogeneous modification

After wet BC particles were solvent-exchanged with pyridine (Py) for three times, 20 and 100 BC particles were modified by succinic anhydrate at 50 °C for 24 h, with DMAP as catalyst and 20 mL of Py as solvent. The conditions and results are shown in Table 2. As shown in Table 2, the succinic anhydrate (SA) amount of sample 17 (14:1 mol/mol AGU) was much higher than that of sample 16 (4:1 mol/mol AGU). However, the DS of sample 17 was 0.16, which was just a little higher than that of sample 16 (DS 0.12). Comparing with the results of homogenous modification, heterogenous reaction resulted in much lower DS.

XRD profiles of BC and SBC

X-ray diffraction (XRD) profiles of BCs and SBCs are shown in Fig. 4. The profiles of BC1 and BC2 are almost same, which means that the crystalline of BC is not affected by the drying method. The profiles of BC1 and BC2 are typical cellulose I XRD pattern [5, 17]. Three main peaks can be identified at $2\theta = 14.5°$, 17°, and

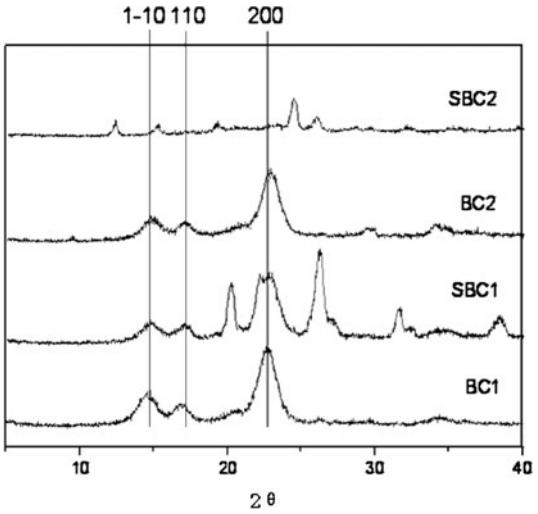

Fig. 4 X-ray diffraction (XRD) profiles of BC and succinylated BC (SBC). *BC1* lyophilizated BC, *BC2* oven-dried BC, *SBC1* heterogenous modified BC, DS 0.16, *SBC2* homogenous modified BC derived from BC2, DS 0.46

22.5°, which is assigned to the (1-10), (110) and (200) reflections planes, respectively. After succinylation, the three peaks of (1-10), (110) and (200) nearly remained in SBC1, which means the heterogenous modification did not change the crystalline of BC. Heterogenous modification should happen on the surface of BC membrane and resulted in low DS, which is in accordance with the results in Table 2. The splitting at (200) and two new strong peaks at $2\theta = 20°$ and 26° in SBC1 pattern should be resulted from new planes caused by succinyl group in the original lattice. However, for homogeneous reaction, dissolution and recrystallization resulted in a new crystalline structure of SBC. The cellulose I pattern disappeared in SBC2, and four new peaks at $2\theta = 12.5°$, 15.5°, 19.5°, and 26° appeared.

Adsorption of Cu^{2+} ion

The adsorption profiles of Cu^{2+} ion onto SBC and BC, as a function of contact time are shown in Fig. 5, where 10 mg BC (or SBC) contacted with 10 mL 0.25 mg/mL $CuSO_4$ solution at pH 4.5 and 28 °C. As shown in Fig. 5, in the first 10 min, adsorbed Cu^{2+} increased sharply, especially on SBC1 and SBC2, being 51.1% and 64.4%, respectively. 30 min later, BC1 and SBC1 almost reached the equilibrium. However, BC2 and SBC2 need longer time to reach their adsorption equilibrium; 90 min is good for SBC2 to get to its equilibrium, getting 84.4% Cu^{2+} adsorbed. For BC2, 120 min is not enough to attain equilibrium. Oven vacuum-dried BC2 is the original material of SBC2. The original material of SBC1 should have similar supramolecular structure with BC1 because both lyophilization and solvent-exchange process could keep the supramolecular structure of original wet BC. The differences of Cu^{2+} adsorption capacity between BCs and SBCs show that SBCs have higher Cu^{2+} binding abilities than their corresponding original BC. For oven

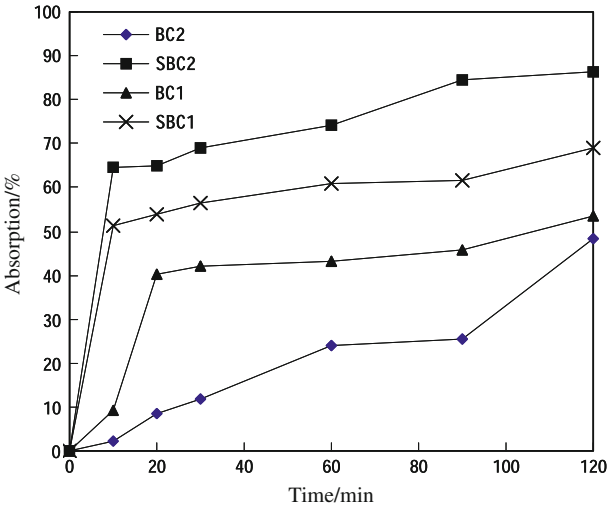

Fig. 5 The plot of Cu^{2+} adsorbed versus contact time (initial concentration of metal ion was 0.25 mg/mL, pH 4.5 ± 0.1, BC (or SBC) 10 mg). *BC1* (*filled triangle*) lyophilizated BC, *BC2* (*filled diamond*) oven vacuum-dried BC, *SBC1* (*times*) heterogenous modified BC (DS 0.16), *SBC2* (*filled square*) homogenous modified BC (DS 0.46), derived from BC2

vacuum-dried BC, the adsorption capacity is lower than that of lyophilizated BC, and it needs longer time to reach equilibrium than lyophilizated BC.

Pseudo-first-order equation (Eq. 4) and pseudo-second-order equation (Eq. 5) were used to investigate mechanism of the adsorption process [18]

$$-\ln\left(1-\frac{q_t}{q_e}\right)=k_1 t \tag{4}$$

$$\frac{t}{q_t}=\frac{1}{k_2 q_e^2}+\frac{t}{q_e} \tag{5}$$

where k_1 is the rate constant of pseudo-first-order adsorption, k_2 is the rate constant of pseudo-second-order adsorption, q_e denotes the amount of Cu^{2+} adsorped at equilibrium, q_t denotes the amount of Cu^{2+} adsorbed at given time.

The values of q_e, k_1, and k_2 can be calculated from the slopes and the intercepts of the straight lines and the data are given in Table 3.

As shown in Table 3, for SBC1 and SBC2, the correlation coefficients for the pseudo-second-order kinetic model are higher than those for the pseudo-first -order kinetic model, being 0.9960, and 0.9982, respectively. Pseudo-second-order kinetic model is more suitable for the Cu^{2+} adsorption mechanism for SBCs, and chemical adsorption is the dominant process. SBCs have higher q_e and adsorption capacity (see Fig. 5) than the original BCs, which expresses that succinylation increased the contact points and binding ability of BC with Cu^{2+}.

Lyophilizated BC (BC1) and vacuum oven-dried BC (BC2) have obvious differences on adsorption of Cu^{2+}. BC2 has lower adsorption amount (q_e) and adsorption capacity (see Fig. 5). Pseudo-first-order kinetic model is more suitable

Table 3 Pseudo-first-order and pseudo-second-order constants and values of R^2 for the adsorption of Cu^{2+} onto BCs and SBCs

Sample	Pseudo-first-order model			Pseudo-second-order model		
	C_0 (mg/mL)	k_1 (min^{-1})	R_1^2	k_2 (g/mg min)	q_e (mg/g)	R_2^2
BC1	0.25	0.0279	0.6863	0.0019	32.82	0.9010
SBC1	0.25	0.0215	0.6214	0.0054	38.74	0.9960
BC2	0.25	0.0131	0.9461	0.0008	18.32	0.7862
SBC2	0.25	0.0342	0.6247	0.0047	49.75	0.9982

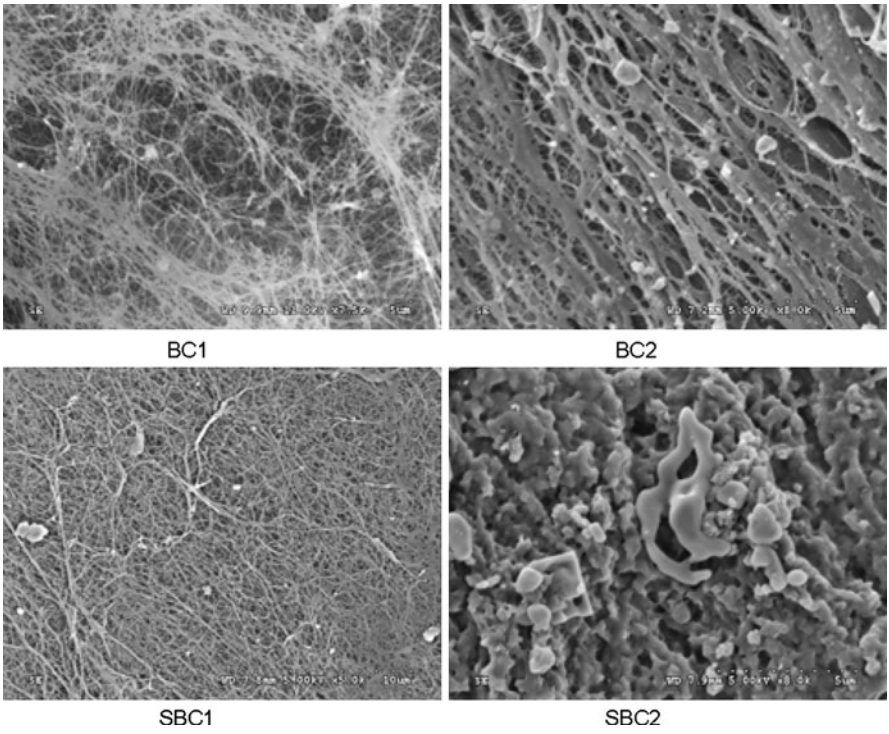

Fig. 6 SEM images of original BC and succinylated BC (SBC). *BC1* lyophilizated BC, *BC2* oven-dried BC, *SBC1* heterogenous modified BC, DS 0.16, *SBC2* homogenous modified BC derived from BC2, DS 0.46

for BC2 (R_1^2 0.9461, while R_2^2 0.7862), which means diffusion is the main controlling step for BC2. According to SEM images in Fig. 6, comparing with BC1, there are smaller micropores on the surface of BC2. Cu^{2+} ions are difficult to diffuse inside BC2 membrane. However, for BC1, the larger micropores result in easy penetration of Cu^{2+} ions to into BC1. Therefore, adsorption of Cu^{2+} ions onto the BC1 fiber becomes the dominant step [19]. The differences between BC1 and BC2 show that morphology of the adsorbent affects the adsorption of Cu^{2+} on BC. SBC1

membrane has much smaller micropores than BC1. SBC2 is powder without obvious micropores. And there are –COOH groups on the surface of SBCs. Therefore, adsorption rather than diffusion is the dominant step for contact between SBCs and Cu^{2+} ions.

Conclusion

Heterogeneous succinylation of BC in pyridine in the presence of DMAP mainly takes place on the surface of BC membrane. Heterogeneous modification results in SBC with low DS and may keep the crystalline structure and mechanical properties of BC. SBCs with different DS from 0.21 to 1.45 were obtained through homogeneous modification in DMAc/LiCl in the presence of triethylamine, which is more practical to get BC derivatives with higher DS and new properties. Both BC and succinylated BC can adsorb Cu^{2+} ion, and the adsorption capacity is affected by both morphology and the amount of –COOH. SBCs show better BC adsorption capacity than their original BCs. BC is a kind of unique cellulose with good resources and special properties. Development of material from BC through chemical modification is a promising field.

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