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Synthesis and characterization of quaternized bacterial cellulose prepared in homogeneous aqueous solution

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ABSTRACT

In this work, bacterial cellulose (BC) was activated by ethylenediamine (EDA) and then dissolved in lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) aqueous solutions. The resulting transparent solution was cast on a glass plate to prepare regenerated BC. Then cationic BC was prepared homogeneously by the reaction between regenerated BC and 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride (CHPTAC) in a NaOH/urea aqueous solution. Structure and properties of the BC and its products were characterized by different techniques such as X-ray diffraction (XRD), Fourier transform spectroscopy (FT-IR), scanning electron microscopy (SEM) and thermo-gravimetric analysis (TGA). The results showed that there was no significant difference between the structures of BC, activated BC and regenerated BC. The effects of different temperature and molar ratio of CHPTAC to anhydroglucose unit (AGU) on the degree of substitution (DS) value were examined. The DS values of cationic BC ranged between 0.21 and 0.51.

1. Introduction

Bacterial cellulose (BC) is a biopolymer of β-1-4-linked glucopyranose molecules, synthesized by various bacteria including *Acetobacter xylinus* and *Acetobacter hansenii* and *Gluconacetobacter xylinum* (Yang et al., 2013). Although BC has the same molecular formula as plant cellulose (PC), it has significantly different structural features and characteristics. In general, BC is more chemically pure, containing no hemicellulose or lignin, which need to be removed during purification of PC. The nano-fibril (~30 nm) networks of BC giving it a much higher surface area and porosity (Shah, Ul-Islam, Khattak, & Park, 2013). Moreover, the degree of polymerization (DP) (200–8000), crystallinity and mechanical strength of BC are higher than that of PC (Shah et al., 2013). BC has been applied for headphone membranes, wound dressing, drug delivery devices, tissue regeneration, catalyst sensing materials, and electrically conductive devices etc. (Klemm, Schumann, Udhardt, & Marsch, 2001; Yoon, Jin, Kook, & Pyun, 2006).

Cationic cellulose ether is one of the most important groups of cellulose derivatives, which has many important properties such as water solubility, chemical stability and non-toxicity. Cationic cellulose ether with amino or ammonium functional groups is widely used in diverse areas such as water treatment, papermaking, chemical, food, cosmetic, and petroleum industries (Prado & Matulewicz, 2014). Especially cationic cellulose ether possessing quaternized groups are effective flocculants in wastewater over a wide range of pH values and shows great promise in water and wastewater treatment. In general, the synthesis of cationic cellulose ether from PC is carried out in water-based solvent systems such as LiOH/urea, NaOH/urea or NaOH/thiourea (Song, He, Jin, & Cheng, 2013; Song, Zhang, Gan, Zhou, & Zhang, 2009; Yan, Tao, & Bangal, 2009), and the alkaline can act as a catalyst for etherification of cellulose (Hebeish, Higazy, El-Shafei, & Sharaf, 2010). Song et al. used PC reacted with 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTAC) in the NaOH/urea aqueous solutions to introduce cationic group (Song et al., 2009). Sirvio, Honka, Liimatainen, Niinimaki, and Hormi (2011) prepared a water-soluble cationic cellulose derivative using dialdehyde cellulose and Girard's reagent T as raw materials. PC with relatively high DP (DP = 500–900) can dissolve in several aqueous alkaline systems, while BC is difficult to dissolve in these solvent systems due to high degree of polymerization (Laszkiewicz, 1998).

BC is insoluble in water and most common organic liquids (Lindman, Karlström, & Stigsson, 2010), and it is also insoluble in

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non-polar solvents, attributing to the strong inter and intra molecular and the high crystallinity (Lindman et al., 2010). Recently, Wada et al. has found that the cellulose I fibrils become swelled as the ammonia or amine molecules penetrate into the crystalline phase of cellulose when BC is immersed in ammonia or amines, and then a crystalline complex with cellulose is formed. After the guest molecules are removed by evaporation or washing, the fibrils deflate and convert into another crystalline form (cellulose III_I) (Wada, Kwon, & Nishiyama, 2008; Wada, Nishiyama, & Langan, 2006). Thus, the accessibility and chemical reactivity of BC can be increased by treatment with liquid ammonia or amines (Wada et al., 2008).

To sum up, many researchers use PC or other soluble cellulose derivatives as raw material and then introduce functional groups to synthesize cationic cellulose under homogeneous conditions. However, cationic cellulose derivatives prepared from BC by a homogeneously process have been scarcely reported because of the insolubility of BC in solvent. In this paper, we reported the homogeneous quaternization of BC in an aqueous solution system. BC was activated by EDA and then dissolved in lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) aqueous solutions and regenerated. The regenerated BC was dissolved in NaOH/urea aqueous solutions directly to prepare a solution, and then CHPTAC was used as etherifying agent homogeneously reacted with regenerated BC in the alkaline condition to prepare cationic BC ether (CBC). The effects of different etherification conditions on the degree of substitution (DS) value were examined.

2. Experimental

2.1. Materials

In this study, BC film was supplied by Hainan Yida Food Industry Co., Ltd, Hainan, China. The BC film was rinsed 5 days with deionized water to reach neutral pH. The BC film was freeze-dried to obtain dry material, and the dried BC film was milled in a Ball milling to pass through a 75-μm sieve. The EDA, DMAc, LiCl and CHPTAC (60 wt%) were purchased from Aladdin Industrial Inc., China. DMAc was dried over 4A molecular sieves, LiCl was dried at 105 °C overnight and then stored in a desiccator before use. All other chemicals in this study were analytical grade and used without further purification.

2.2. Activation of BC

5 g of BC was dispersed into 360 g of EDA solution, and then stirred for 90 min at 45 °C. After the reaction, the solution was separated by filtration, and then filter residue (activated BC, ABC) was washed with distilled water and dried in a vacuum oven at 80 °C for 24 h.

2.3. Preparation of regenerated BC

97 g of LiCl/DMAc solution (the value of LiCl was about 9%, w/w) was added to a flask with a magnetic stirrer. The mixture was heated at 95 °C for 30 min. After that, 3 g of ABC was added into that solution. The dispersions were heated at 95 °C for 3 h, with a fast stirring. The dispersion was made to stand for one night at room temperature. Then the dispersion was stirred at room temperature for 30 min to form homogeneous and transparent BC/LiCl/DMAc solution, and the above mixture was poured and cast onto the glass plate to obtain regenerated BC (RBC) film. Subsequently, the films were soaked into the water to remove the residual LiCl/DMAc completely until the weight got constant, followed by dried in an oven at 80 °C under vacuum for 24 h to obtain RBC.

2.4. Preparation of homogeneous RBC solution

RBC solution was prepared according to the method described previously (Qi, Yang, Zhang, Liebert, & Heinze, 2011). 2 g of RBC was mixed with 49 g 14 wt% NaOH aqueous solution pre-cooled to 0 °C. The mixtures were stirred for 1 min. Then, 49 g 24 wt% urea aqueous solution pre-cooled to 0 °C was poured immediately into it with vigorous stirring for 2 min at 0 °C. Within this time, a transparent RBC solution was obtained, and then a modest centrifugal separation (2500 rpm for 15 min at 10 °C) was applied to remove the insoluble part from the RBC solution. The mass fraction of BC was adjusted to 1.5 wt% using 7 wt% NaOH–12 wt% urea aqueous solution.

2.5. Synthesis and purification of CBC

70 g of CHPTAC aqueous solution (60 wt%) was added dropwisely into the 150 g RBC solution obtained previously. After all of the CHPTAC had been added, the mixture was stirred at 45 °C for 12 h, the sample was neutralized with aqueous acetic acid and then dialyzed with regenerated cellulose bag (M_w cutoff 8000) against distilled water for about 7 days. The solution was finally freeze-dried to obtain the purified CBC. Solubility of the CBC in distilled water was measured at 25 °C, and the CBC concentration was about 1% (w/v).

2.6. X-ray diffractometer (XRD)

The samples were pressed into disks and analyzed by a X'Pert Pro MPD (PANalytical B.V., Holland) diffractometer with Ni-filtered CuKα radiation ($\lambda = 0.1541$ nm) generated at 40 kV and 20 mA. The XRD were recorded from 0° to 80° at a scanning speed of 1°/s and sampling rate of 2 data/s. The crystallinity index (CI) was determined according to the Segal method (Segal, Creely, Martin, & Conrad, 1959). The CI was calculated according to the following equation:

$$CI = \frac{I_{002} - I_{\mathrm{am}}}{I_{002}} \times 100\% \quad (1)$$

where I_{002} is the maximum intensity of the diffraction from the (0 0 2) plane at $2\theta = 22–23°$, and I_{am} is the intensity of the amorphous background scatter measured at $2\theta = 18–19°$ where the intensity is minimum.

2.7. The degree of polymerization (DP)

The degradation degree of RBC during the reaction was determined by DP value of sample: the sample was diluted with an excess of ethanol, the residue was separated by filtration, and then rinsed thoroughly with distilled water to remove the cationic products.

The DP of the samples was determined according to McCormick, Callais, and Hutchinson (1985) applying LiCl/DMAc as solvent, and the DP value of samples was calculated from the intrinsic viscosity.

2.8. Elemental analysis

Nitrogen contents (N%) of samples were determined with an elemental analyzer (VARIO EL cube, Elemental Analysis System Co. Ltd., Germany), and the degree of substitution (DS) was calculated from nitrogen analysis according to the following equation (Song et al., 2009):

$$DS = \frac{162.5\ \mathrm{N\%}}{1401 - 151.64\ \mathrm{N\%}} \quad (2)$$