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Preparing cationic cotton linter cellulose with high substitution degree by ultrasonic treatment

Fulong Zhang[a], Zhiqiang Pang[a], Cuihua Dong[a,*], Zong Liu[b]

[a] Key Laboratory of Pulp & Paper Science and Technology, Qilu University of Technology, Jinan 250353, China
[b] Department of Biological Systems Engineering, University of Wisconson, Madison, WI 53706, USA

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ABSTRACT

As an important cellulose derivative, cationic cellulose has becoming an attractive material. However, it remains challenging to produce cationic cellulose with high substitute degree. In this paper, we successfully increased the substitute degree of cationic cellulose by introducing ultrasonic treatment, which efficiently breaks hydrogen bonds of the chemical structure of cationic cellulose. Properties of cationic cellulose were studied by scanning electron spectroscope (SEM), contact angle, X-ray diffraction (XRD) and thermogravimetric analysis (TGA). Experimental results show that the cationic cellulose has rougher surface and lower crystallinity degree as compared to the original sample. TGA analysis verifies that the thermostability of CLC decreases after the cationic modification. The residual of the cationic cellulose (25 wt%) after pyrolysis increases significantly as compared to that of the original cellulose (15 wt%).

1. Introduction

As the most abundant natural polymer, cellulose has received broad attention attributed to its renewability, sustainability and biodegradability (Shi, Zhang, Qin, & Chen, 2010). Previously, cellulose and its derivatives were demonstrated to be potential sustainable production of chemicals and fuels (Binder & Raines, 2009; Dhepe & Fukuoka, 2008). For example, cellulose derivatives based on anionic groups have been reported to be used as drug encapsulation and release (Trygg, Yildir, Kolakovic, Sandler, & Fardim, 2014); Cellulose nanofibers have been adopted to prepare hydrophobic aerogels for oil superabsorbent (Zhang, Sèbe, Rentsch, Zimmermann, & Tingaut, 2014). Cellulose nanocrystals have been employed as rheology and fluid loss modifiers in water-based drilling fluids (Li, Wu, Song, Qing, & Wu, 2015). However, due to the existence of many intra- and inter-molecular hydrogen bonds in its chemical structures, cellulose is hardly soluble in most solvent systems, resulting in the limited development and utilization of its derivatives (Kulpinski, Erdman, Namyslak, & Fidelus, 2012). Chemical modification can extend cellulose's functionality, and thus broaden its application scope. A tremendous amount of efforts have been made to understand the nature of cellulose, cellulose derivatives, cellulose composites, as well as cellulose copolymers and blends. Currently, cellulose derivatives can be successfully produced based on esterification and etherification of hydroxyl groups on cellulose. Some of these cellulose derivatives have been commercially applied in large-scale production (Wu & Kuga, 2006).

Being an important cellulose derivative, cationic cellulose has been successfully applied in cosmetic, paper additives, adsorbents and antibacterial agents (Rodríguez, Alvarez-Lorenzo, & Concheiro, 2003; Baiardo, Frisoni, Scandola, & Licciardello, 2002). Previously, a small dosage (0.15 wt%) of cationic cellulose was demonstrated to be more efficiently than traditional drainage aid in improving the physical strength of old newspaper and the drainability of pulping slurry (Gruber & Weigert, 1998). Cellulose nanocrystals (CNCs) have gained increasing attention for cationic modification in the material community. Their unique chemical and mechanical properties, especially large surface area with high accessibility enable high density of substituents, and a variety of functional groups, including pyridinium (Jasmani, Eyley, Wallbridge, & Thielemans, 2013), quaternary amine (Zhu et al., 2014; Rosilo et al., 2014; Zaman, Liu, Xiao, Chibante, & Ni, 2013; Salajková, Berglund, & Zhou, 2012), poly(2-aminoethylmethacrylate), poly[*N*-(2-aminoethylmethacrylamide)] (Hemraz et al., 2015), poly[2-(dimethylamino)ethyl methacrylate] (Tang et al., 2014), polyamidoamine dendrimer (Tehrani & Basiryan, 2015) and poly(4-vinylpyridine) (Kan, Li, Wijesekera, & Cranston, 2013) have been successfully covalently bonded to CNCs. And the cationic CNCs could found a wide range of applications, such as sorbent (Zhu et al., 2014), biodegradable flocculants (Kan et al., 2013) and

* Corresponding author. Tel.: +86 053189631168.
E-mail addresses: zfl363@126.com (F. Zhang), zhiqiang8508@126.com (Z. Pang), xiaodong771111@163.com (C. Dong), zliu73@wisc.edu (Z. Liu).

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surface finishing agent (Zaman et al., 2013). Introducing quaternary ammonium salt by etherification is usually preferred in preparing cationic cellulose. However, previous researches on cationization of cellulose mainly focused on exploitations of cationic reagents, which limits the cationization degree (Hasani, Westman, Potthast, & Rosenau, 2009). Moreover, since hydroxyl groups in cellulose readily form network of hydrogen bonds, reactivity of cellulose was significantly retarded (Pang, Chen, Dong, Yang, & Liu, 2013). For higher cationization degree, we propose to use ultrasound energy as an effective tool to improve the reactivity of hydroxyl groups of cellulose in this paper.

Ultrasound energy can be transferred to reactants by the cavitation process, which involves formation, growth and violent collapse of cavities in solvent (Ji, Wang, Li, Yu, & Xu, 2006; Santos, Malveira, Cruz, & Fernandes, 2010). The energy provided by cavitation (10–100 kJ/mol) remains on the level of hydrogen bond energy. Thus, ultrasonication is particularly effective in enhancing reactivity of hydroxyl groups in cellulose by breaking hydrogen bonds and improving mass transfer properties. To the best of our knowledge, cationization of cotton cellulose with high crystallinity assisted by ultrasonic treatment has not been explored yet. In this work, we investigated the high degree of substitution of cotton cellulose with quaternary ammonium salt using assisted ultrasonic treatment. Experimental results and analysis demonstrated that cationic CLC with high degree of substitution can be successfully prepared by ultrasonic treatment.

2. Materials and methods

2.1. Materials

2,3-Epoxypropyltrimethylammonium chloride (EPTC) was purchased from Shanghai Chemicals Inco., and cotton linter cellulose (CLC) was obtained from Shanhe Pharmaceutical Inco. All the other chemicals were used as received without further purification.

2.2. Pretreatment of CLC

Before the cationic modification, the CLC was pretreated with 40 wt% sulfuric acid at room temperature for 24 h and washed thoroughly with distilled water. Then the pretreated cellulose was vacuum dried at 50 °C for 48 h.

2.3. Preparation of cationic CLC

The pretreated CLC was dispersed into 10 wt% NaOH and stirred for 10 h at room temperature. Then, EPTC (molar ration of 3:1 with anhydroglucose unit in CLC) was added, and the mixture was stirred in ultrasonic processor (KQ-300E, Kunshan Shumei Inco., China, 40 KHz, and 300 W) at 80 °C. After various residence time of cationic modification, the samples were filtered and thoroughly washed with distilled water, and then vacuum dried at 50 °C for 48 h.

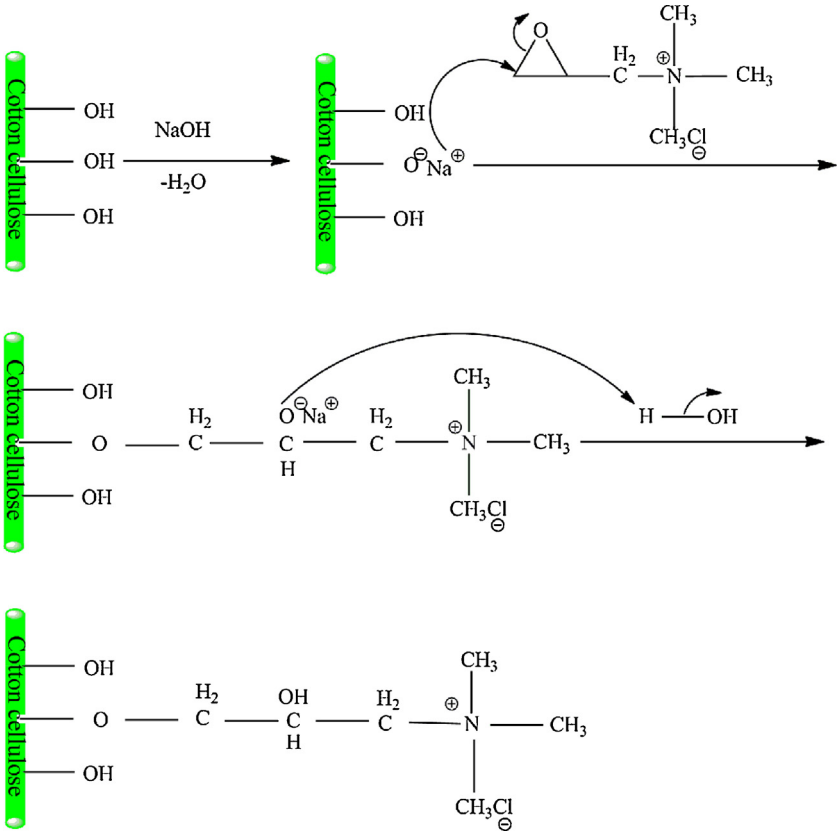
2.4. Determination of substitution degree (DS)

The DS of quaternary ammonium groups was determined by the nitrogen content (X_N) of cationic CLC according to following equation:

$$DS = \frac{(162.15 \times X_N)}{(14 - 151.63 \times X_N)} \quad (1)$$

where X_N is the amount of nitrogen in cationic CLC in weight percentage, 162.15 is the molecular weight of anhydroglucose unit, and 151.63 is the molecular weight of the substituted group.

The nitrogen content of cationic CLC was calculated by elemental analysis using a Carlo Erba EA 1108 CHNS analyzer. Elemental



Scheme 1. Cationization reaction of hydroxyls in CLC.