



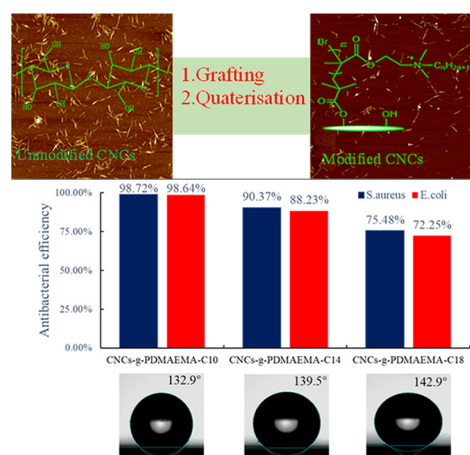
# Effect of surface wettability on the antibacterial activity of nanocellulose-based material with quaternary ammonium groups

Ming Li, Xiaohong Liu, Ning Liu, Zihe Guo, Puneet Kumar Singh, Shiyu Fu\*

State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China



## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

Cellulose nanocrystals  
Antibacterial  
Hydrophobic  
Quaternary ammonium groups

## ABSTRACT

Cellulose nanocrystals (CNCs) is a kind of natural, renewable, and biocompatible materials that can be functional via the surface modification. A covalently bonded CNCs-g-PDMAEMA was prepared by grafting 2-(dimethyl-amino) ethyl methacrylate (DMAEMA) on the CNCs' surface via atom transfer radical polymerization (ATRP). Subsequently, the tertiary amino groups of the CNCs-g-PDMAEMA were transferred to quaternary ammonium groups by adding alkyl bromides with different carbon chain lengths (C10-C18). It was found that the antibacterial activity of the prepared materials is related to the quaternary group structure. The material containing C10 alkyl in quaternary group exhibited the best antibacterial efficiency, which was closely associated with the wettability of the quaternary CNCs-based polymers. The lower wettability of materials with higher hydrophobicity may impose a restriction on the polymeric antibacterial groups' accessibility to the cytoplasmic membrane of bacteria. The antimicrobial CNCs-based composites may be potential to apply as coating agents for aseptic packaging.

## 1. Introduction

Cellulose nanocrystals (CNCs) are typically prepared by acid

hydrolysis from cellulosic materials [1]. CNCs possess excellent physicochemical properties including mechanical strength [2], specific surface area [3], transparency [4] and crystallinity [5,6]. They are also

\* Corresponding author.

E-mail address: [shyfu@scut.edu.cn](mailto:shyfu@scut.edu.cn) (S. Fu).

biodegradable and biocompatible materials, attracting much attention in the field of medicine [7–10] and food packaging [11]. However, the CNCs retain the macromolecular structure of nature cellulose, i.e. chains of  $\beta$ -1,4-linked glucopyranose units crystallized by inter- and intra- hydrogen bonds. Such structures are readily digested by environmental microorganisms, which requires the CNCs inactive to microbial contaminants when used in functional packaging materials.

With resourceful hydroxyl groups on their surface, CNCs can be functionalized through chemical modification. Several methods have been reported for the CNCs surface modification, such as oxidation [12,13], esterification [14], silanization [12,15], and polymer grafting [16]. Among these methods, modification with quaternary ammonium can efficiently promote the antimicrobial activity of cellulose. Till now, various quaternary ammonium salts have been studied for this purpose [15,17,18]. For example, glycidyltrimethylammonium chloride (GTMAC) was used to graft to the surface of CNCs via ring-opening reaction. The products were good for removal of anionic azo dye [18]. The same approach was also applied to prepare antibacterial films based on quaternized cellulose [19,20]. The blend films based on polyvinyl alcohol/quaternized cellulose exhibited higher tensile strength, higher thermostability, lower water permeability, and especially, higher antibacterial activity [20]. Recently, cellulose-based antibacterial membranes have been prepared via alkoxy silane polycondensation [15]. Covalently-linking the hydroxyl groups of microfibrillated cellulose by esterification could generate non-leaching antimicrobial agents [14]. To increase the active sites in CNCs, 2,2,6,6-Tetramethylpiperidine-1-oxyl radical (TEMPO) oxidation was successfully utilized to introduce a large number of carboxyl on backbone [21]. Therefore, it is reasonable to develop hydrophobic biocomposites with quaternary ammonium moieties from the TEMPO-oxidized CNCs [22].

Atom transfer radical polymerization (ATRP) is one of the most versatile and powerful technology to synthesize functional macromolecules. It may facilitate the control of length of polymer chains, and, thereby, tailors the properties of the surface [23], and could be used for synthesis of block copolymer grafts with uniform Mw distribution [16,24]. Surface-initiated ATRP has also been reported for the grafting of well-defined functional polymers from a variety of substrates including CNCs [23–27].

In this study, we developed a CNCs based antibacterial material by the beforehand esterified-CNCs polymerizing with DMAEMA via surface-initiated ATRP. The interesting finding is that the antibacterial efficiency is related to the wettability of materials with quaternary group containing different carbon chain lengths, which will provide a better understanding to the effect of wettability of quaternary group on antibacterial efficiency of materials.

## 2. Experimental

### 2.1. Materials

2-Bromoisobutyl bromide (BIBB, 98%, Aladdin), N-methy-2-pyrrolidone (NMP, 99%, Aladdin), 2-(Dimethyl amino) pyridine (DMAP, 99%, Aladdin), N, N, N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%, Aladdin) and N, N-dimethylformamide (DMF, AR, Tianjin, China) were dried on molecular sieves (4A<sup>+</sup>) for more than three days before use. CuBr (99%, Energy Chemical) was purified by stirring in glacial acetic acid, filtered, washed with ethanol three times, and then dried overnight in a vacuum at room temperature. Triethylamine (TEA, AR, Tianjin, China), 2-(dimethylamino) ethyl methacrylate (DMAEMA, 99%, Aladdin), 1-bromodecane (98%, Aladdin), 1-bromotetradecane (99%, Aladdin) and 1-bromooctadecane (97%, Aladdin) were used without further purification. *Escherichia coli* and *Staphylococcus aureus* were purchased from the Guangzhou Institute of Microbiology. CNCs were prepared following the reported method [28].

### 2.2. Synthesis of ATRP macro-initiator

The ATRP macro-initiator, CNCs-IBBr, was prepared according to the reference method with modification [25,29]. DMAP (0.02 mol) and TEA (0.03 mol) were added in a 250 ml flask, containing 200 ml NMP and 3.24 g pretreatment of CNCs (active hydroxyl groups 0.06 mol). The mixture was stirred in an ice-water bath with protection of Argon. Then, BIBB (0.12 mol) was dropwise added to the reaction mixture. After 24 h, the product was thoroughly washed with ethanol, and then extracted with water: ethanol (1:1, v/v) for 12 h. Finally, the sample was freeze-dried and weighed. The weight of CNCs-IBBr was used to calculate the degree of substitution (DS, the average number of reacted hydroxyl groups per glucose units of cellulose [30]) in the esterification.

### 2.3. ATRP of DMAEMA using CNCs-IBBr as the initiator

The CNCs-IBBr macro-initiator was used to initiate the polymerization of DMAEMA on the surface of CNCs by ATRP with CuBr/PMDETA. CNCs-IBBr (0.4 g) was placed in a flask containing DMF (30 ml), DMAEMA (7.85 g, 0.05 mol), CuBr (0.144 g, 0.001 mol), PMDETA (0.171 g, 0.001 mol). The reaction system was then executed with three freeze-evacuate-thaw cycles. The polymerization was carried out at 60 °C for 24 h under stirring. The product, CNCs-g-PDMAEMA, was thoroughly washed to remove unreacted agents, finally freeze dried and weighed. Graft yield and graft efficiency in this step were calculated using Eqs. (1) and (2).

$$\text{Grafting yield (GY)} = (W_p - W_{\text{CNCs-IBBr}}) / W_{\text{CNCs-IBBr}} \times 100\% \quad (1)$$

$$\text{Grafting efficiency (GE)} = (W_p - W_{\text{CNCs-IBBr}}) / W_M \times 100\% \quad (2)$$

Where,  $W_p$ ,  $W_{\text{CNCs-IBBr}}$  and  $W_M$  are the weight of CNCs-g-PDMAEMA, CNCs-IBBr and monomer, respectively.

### 2.4. Quaternization of CNCs-g-PDMAEMA

The CNCs-g-PDMAEMA polymer was quaternized with reagents of 1-Bromodecane, 1-Bromotetradecane and 1-Bromooctadecane, respectively. 0.3 g of CNCs-g-PDMAEMA was reacted with excess amount of reagent (2.0 g) under stirring in Ar. Then, the crude product was washed and extracted with ethanol before characterization. The quaternized CNCs-g-PDMAEMA was termed as CNCs-g-PDMAEMA-Cn (n = 10, 14, 18). The degree of quaternary (QD) was used to evaluate this reaction, and was defined as the percentage of reacted tertiary amine on CNCs-g-PDMAEMA (Eq. (3)).

$$\text{QD} = ((W_Q - W_p) / M_{\text{CnBr}}) / (W_p \times 7.72\% / 14) \times 100\% \quad (3)$$

Where,  $W_Q$  and  $W_p$  are the dry weights of CNCs-g-PDMAEMA before and after quaternization, respectively.  $M_{\text{CnBr}}$  and 14 are the molar mass of quaternary agent and nitrogen, respectively. 7.72% is the content of nitrogen in CNCs-g-PDMAEMA, as seen in Table 1. The weight and QD of CNCs-g-PDMAEMA-C10, CNCs-g-PDMAEMA-C14 and CNCs-g-PDMAEMA-C18 are shown in Table 1.

**Table 1**  
Elemental analysis result and the weight of the samples.

Samples	C (%)	H (%)	N (%)	W (g)	QD (%) <sup>b</sup>
CNCs-IBBr <sup>a</sup>	40.34	6.08	0.25	3.96	–
CNCs-g-PDMAEMA	57.08	8.44	7.72	4.00	–
CNCs-g-PDMAEMA-C10	49.80	8.87	3.46	0.52	60.19
CNCs-g-PDMAEMA-C14	53.36	9.51	3.19	0.59	63.30
CNCs-g-PDMAEMA-C18	56.48	9.80	2.88	0.67	67.18

<sup>a</sup> Bromine content in the CNCs-IBBr was 8.88%, and the DS of the CNCs-IBBr was 0.22.

<sup>b</sup> Determined by the Eq. (3).

Download English Version:

<https://daneshyari.com/en/article/6977205>

Download Persian Version:

<https://daneshyari.com/article/6977205>

[Daneshyari.com](https://daneshyari.com)