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Preparation and characterization of durable antibacterial cellulose biomaterials modified with triazine derivatives

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ABSTRACT

Cellulose fabric was chemically modified with the triazine derivatives containing the multi-cationic benzyl groups. The novel durable antibacterial cellulose biomaterial containing the multi-cationic benzyl groups was prepared. The chemical structure and thermal property of the antibacterial cellulose biomaterial were investigated with FT-IR spectra, nitrogen content analysis, and differential scanning calorimetry (DSC). The results show that the thermal stability of the novel antibacterial cellulose was slightly decreased. Physical properties of the novel antibacterial cellulose had not significant change. The novel antibacterial cellulose imparted excellent durable antibacterial properties.

1. Introduction

In recent years, the threat of potentially harmful bacteria and viruses stresses the importance of developing materials to combat human pandemics. The cellulose fiber is one of the excellent natural materials that have wide application in different production. Much attention has been paid on utilization of the cellulose, due to its good biodegradability, biocompatibility and nontoxicity. Cellulose has been also explored as a substrate for composite materials because of the presence of several functional groups that may be employed in various activation processes (Fu, Hsiao, Pagola, Stephens, et al., 2001; Kulpinski, 2005; Xie, Sun, & Hou, 2006, 2007). However, the cellulose fibers provide an excellent environment for microorganisms to grow, because of their large surface area and ability to retain moisture. A number of chemicals have been employed to impart antimicrobial activity to the cellulose materials (Adamopoulos et al., 2007; Barud et al., 2008; Maneerung, Tokura, & Rujiravanit, 2008). Those chemicals include inorganic salts, organometallics, iodophors, phenols and thiophenols, onium salts, heterocyclics with anionic groups, nitro compounds, formaldehyde derivatives, and some amines. Many of these chemicals, however, are toxic to human and do not easily degrade in the environment.

The excellent fabrication of antimicrobial surfaces must be very biocompatible, i.e., they must not be harmful to humans. They also must maintain their antimicrobial activity under a variety of environmental conditions, and are not removed upon washing. Thus far, very few antibacterial materials meet the above criteria. A number of attempts have been made to modify the cellulose fiber using the compounds containing the certain groups (Schramm, Bischof, & Katovic, 2002; Xie, Hou, & Wang, 2008; Xie, Hou, & Zhang, 2006). One of the research efforts in the area demonstrates that N-alkylated poly (4-vinyl-pyrdine) groups can create the surfaces killing wild-type and antibiotic-resistant bacteria (Lee et al., 2004; Lin, Lee, Lewis, & Klibanov, 2002). Similarly, some reports discover that amine-derivatized carbohydrates (cotton, bulk cellulose, paper, gauze, chitosan) are surface active against a variety of both gram positive and negative bacterial strains. Some nanofibers impart good antibacterial properties. The nanofibers can be made by continuous electrospinning. The mathematical models of electrospinning are given (He, Xu, Wu, & Liu, 2007; Wang, He, & Xu, 2008). Dodecyl dimethylbenzyl ammonium chloride (1227) is an important antibacterial agent. The materials treated with dodecyl dimethylbenzyl ammonium chloride impart excellent antibacterial activity because of benzyl cationic group. However, those materials are easy to lose antibacterial activity after washing. The exposed long chain ammonium functionality on the surface of the materials kills a gamut of bacteria on simple contact, and do not lose activity upon prolonged use. The mechanism of activity is postulated to be purely physical in nature and to rely on the dynamic interaction of the surface with the cell wall of the bacteria. As a result, the bacteria cannot resort to any protective or immunological response mechanisms for survival (Lim & Hudson, 2004; Lu et al., 2001; Wang, Du, & Liu, 2004).

In this paper, cellulose material is chemically modified with the triazine derivatives containing the multi-cationic benzyl groups. The molecular chains of modified cellulose biomaterial have both cationic and long carbon-chain groups. The incorporation of

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multi-cationic and long carbon-chain groups may improve antibacterial activity. The chemical structure is shown in Scheme 1.

The reports of the bio-cellulose modified with the triazine derivatives containing the multi-cationic and benzyl groups are scarce. The chemical structure and thermal properties of the modified cellulose biomaterial are investigated with FT-IR spectra, differential scanning calorimetry (DSC) and the nitrogen content. The antibacterial activity and physical properties of the cellulose biomaterial are also discussed.

2. Experimental

2.1. Materials

Desized, scoured and bleached cellulose fabrics were obtained from Jinqiu Textile and Finishing Company, Shaoxing, China. The 1,3,5-triazine derivative containing the reactive groups, 2,4,-bi [(3-benzyl-3-bimethylammonium) propylamino]-6-choro-1,3,5-triazine chloride (BBCTC), was obtained from National Engineering Research Center for Dyeing and Finishing of Textiles, Shanghai, China. Other chemicals used were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

2.2. Modification to cellulose fabric with the triazine derivatives containing the multi-cationic groups

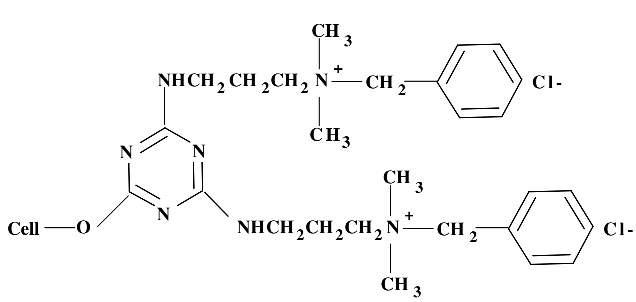
The 1,3,5-triazine derivative containing the reactive groups, 2,4,-bi [(3-benzyl-3-bimethylammonium)propylamino]-6-choro-1,3,5-triazine chloride (BBCTC) was dissolved in distilled water to give the 8% solution by weight. To the solution was added 1.5% sodium hydroxide by weight as catalyst. Samples of cellulose, 5 g, were treated with 100 ml the solution in the dyeing machine. The samples were kept at 40 °C for 8 h. The modified fabrics were then washed with tap water until neutral and again washed in warm water(60 °C) using a domestic washing machine to remove unfixed compounds. The fabrics were dried at ambient conditions.

2.3. FT-IR spectra

FT-IR spectrum of the sample was measured by an OMNI Sampler of the Nexus-670 FT-IR-Raman Spectrometer (Nicolet Analytical Instruments, Madison WI), using a single ART reflecting method.

2.4. Nitrogen content

The nitrogen content was determined by Elementar Vario(III) (Germany). The samples were dried under vacuum at the temperature of 50 °C before measuring.



Scheme 1. Chemical structure of the modified cellulose.

2.5. DSC

A DSC 822e differential scanning calorimeter (Mettler/Toledo, Greifensee, Switzerland) was used. Samples of about 5 mg, placed in a DSC pan, were heated from 25 to 425 °C at a scanning rate of 10 °C/min, under a constant flow of dry nitrogen.

2.6. Physical property measurements

Fabric tensile strength was determined by using a H10KS Tensile Testing Machine (Hounsfield SDL Co.). Six specimens (three for warp and three for weft) were tested at a gauge length of 200 mm with a stain rate of 30 mm/min. The width of the specimen was 50 mm. The tensile and tear properties of the fabric were measured according to ISO13934.1:1994 and ISO 13937.1:1995, respectively.

The conditional wrinkle recovery angle (WRA) was measured by using a P500570 (SDL. Co.) according to AATCC Test Method 66-2003.

2.7. Antibacterial activity assay

Antibacterial activity of the novel bio-cellulose against *Staphylococcus aureus* (ATCC 6538) was evaluated by ASTM E2149-01. The test method was designed to evaluate the resistance of non-leaching antimicrobial treated specimens to the growth of microbes under dynamic contact conditions. *S. aureus* was used as a test organism. The modified bio-cellulose materials and control (blank cellulose) samples (0.75 g, respectively) were cut into small pieces and transferred to a 250 ml Erlenmeyer flask containing 50 ml of the working bacterial dilution. All flacks were capped loosely, and placed on the incubator, and shaken for 1 h at 37 °C and 120 rpm using an incubator shaker. After a series of dilutions of the bacterial solutions using the buffer solution, 1 ml of the dilution was plated in nutrient agar. The inoculated plates were incubated at 37 °C for 2 days and surviving cells were counted.

The antibacterial activity was expressed in terms of percentage reduction of the organism after contact with the test specimen compared to the number of bacterial cells surviving after contact with the control. The percentage reduction was calculated using the following equation,

$$R(\%) = \frac{B - A}{B} \times 100$$

where A and B are the surviving cells (colony forming unit CFU/ml) for the flasks containing test samples and the control (blank cellulose), respectively, after 1 h contact time. *R* (%) is the percentage reduction.

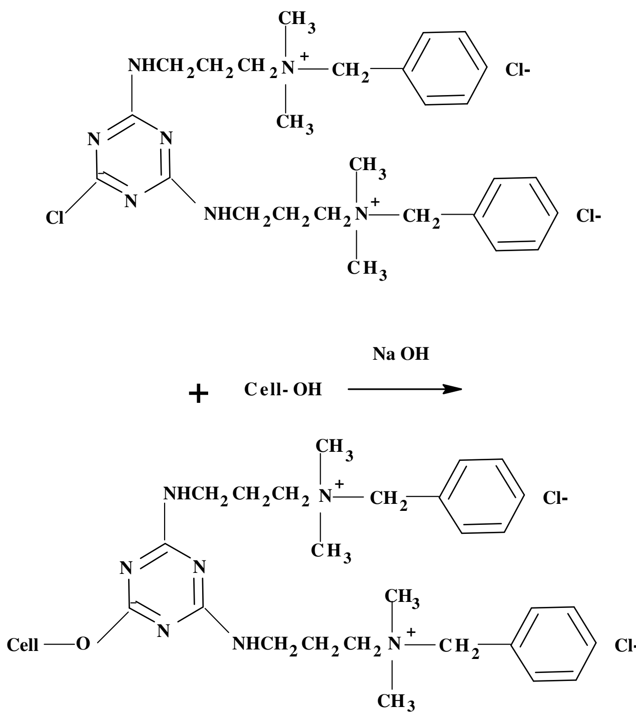
2.8. Washing cycle

The modified fabrics were washed using a domestic washing machine in warm water (40 °C) for 15 min, then were washed using a domestic washing machine in cold water for 15 min. The fabrics were dried at ambient conditions.

3. Results and discussion

3.1. Chemical modification of cellulose with the triazine derivative BBCTC

The molecular structure of cellulose has a lot of hydroxyl. The compound 2,4,-bi [(3-benzyl-3-bimethylammonium)propylamino]-6-choro-1,3,5-triazine chloride (BBCTC) is able to form



Scheme 2. Reaction of BBCTC with cellulose.

covalent bonds with cellulose under alkaline conditions (NaOH as catalyst). The reaction is shown in Scheme 2.

The macromolecular chains of the modified cellulose have multi-cationic benzyl groups (Scheme 3). FT-IR spectra of the unmodified and modified cellulose are shown in Figs. 1 and 2, respectively. FT-IR spectra of the modified cellulose assured the presence of —N=C at 1593 cm^{-1} (1,3,5-triazine cycle).

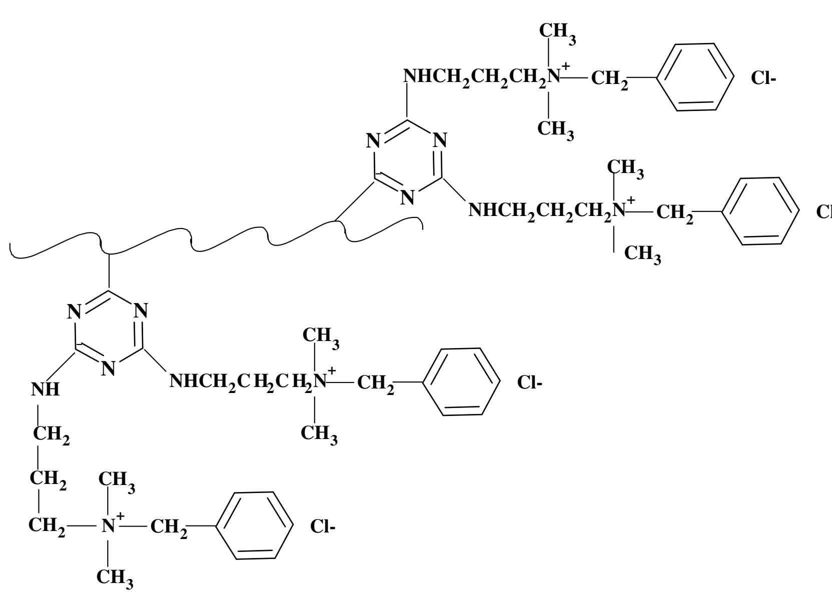
The nitrogen contents of the unmodified and modified cellulose were determined (shown in Table 1). Compared with the unmodified cellulose, the nitrogen content of the modified cellulose increased. This confirms that the compound BBCTC were able to form covalent bonds with cellulose. The modified cellulose biomaterial containing multi-cationic groups was achieved.

3.2. Thermal properties of the novel antibacterial cellulose containing the multi-cationic groups

The thermal properties of cellulose are crucial important in many applications, due to their strong influence on durable and oxidation characteristics of the materials. Differential scanning calorimetry (DSC) is one of important methods for observing the thermal characteristics of materials. After cellulose fabric was chemically modified with 2,4,-bi [(3-benzyl-3-bimethylammonium)propylamino]-6-choro-1,3,5-triazine chloride (BBCTC), the chemical modification had an effect upon the thermal stability of the modified cellulose. The DSC plots of the unmodified and modified cellulose with 2,4,-bi [(3-benzyl-3-bimethylammonium) propylamino]-6-choro-1,3,5-triazine chloride (BBCTC) were shown in Figs. 3 and 4, respectively. For the unmodified cellulose, the endothermic peak initiated at 321.56 °C, finished at 375.73 °C. For the modified cellulose containing multi-cationic groups, the endothermic peak initiated at 319.69 °C, finished at 373.38 °C. Moreover, the modified cellulose exhibited major endothermic peak at 354.79 °C. The position of the endothermic peak of the modified cellulose was lower 6.17 °C than that of the unmodified cellulose. The endothermic changes obtained in the DSC plot for cellulose are associated with decomposition processes, which may occur within the fabric during heating. The endothermic peaks occurring in the DSC plots for both unmodified and modified cellulose fabrics are possibly due to local changes either in the crystalline regions of natural cellulose or a breakdown in the modified cellulose on heating. This phenomenon shows that the thermal stability of the modified cellulose slightly decreased.

3.3. Physical properties of the novel antibacterial cellulose containing the multi-cationic groups

Physical properties of the cellulose fabric treated with the certain groups or compounds may be changed. For example, cellulose to which crosslinking has been introduced has improved elastic recovery due to the inhibition of slippage between the molecules when forces are applied. In our recent research work, physical properties of the net modified cellulose fabric with a 1,3,5-triazine derivative containing the multi reactive groups have been changed (Xie, Sun et al., 2006; Xie et al., 2008). Physical properties of the novel antibacterial cellulose containing the multi-cationic groups



Scheme 3. The structure of cellulose modified with multi-cationic benzyl groups.

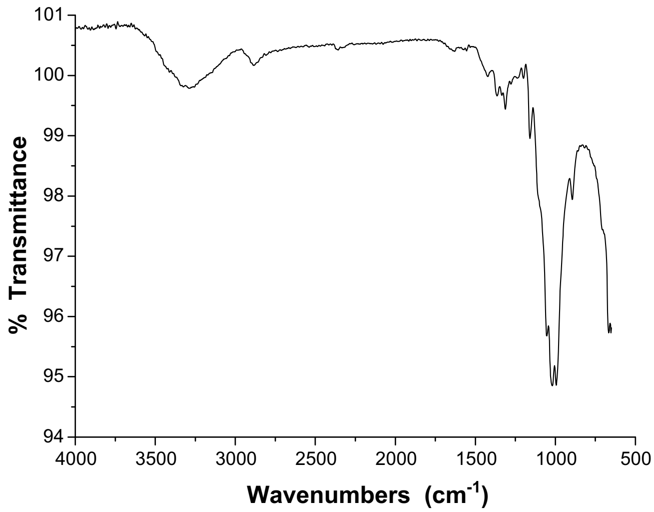


Fig. 1. FT-IR spectrum of the unmodified cellulose.

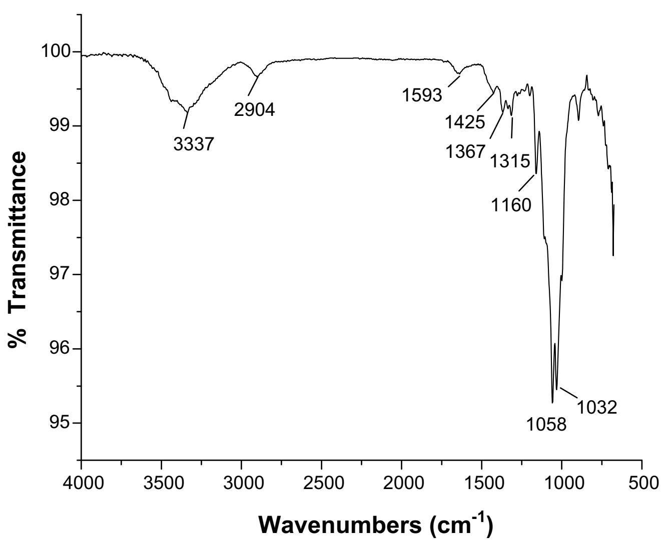


Fig. 2. FT-IR spectrum of the modified cellulose.

Table 1
Analysis of the nitrogen content

	Unmodified cellulose	Bio-cellulose
N(%)	0.337	0.469

were investigated. The tensile, the wrinkle recovery angle (WRA) and tearing strength of the untreated and treated cellulose fabrics are presented in Table 2, respectively.

Table 2 indicates that compared with the untreated cellulose fabric, the tensile strength of the modified cellulose with multi-cationic groups showed a slight decrease. The WRA of the treated cellulose fabric had very slight improvement. It is found that the bio-cellulose fabric had not significant influence on the physical properties.

3.4. Antibacterial properties of the cellulose fabric containing the multi-cationic groups

Many biochemical properties of materials are dependent on the surface chemical structure. Chemical modification of cellulose can change itself chemical and morphological structures. The cellulose material was chemically modified with triazine derivatives containing the multi-cationic benzyl groups. The molecular chains of the modified cellulose biomaterial had both cationic and long carbon-chain groups. Antibacterial activities of the modified

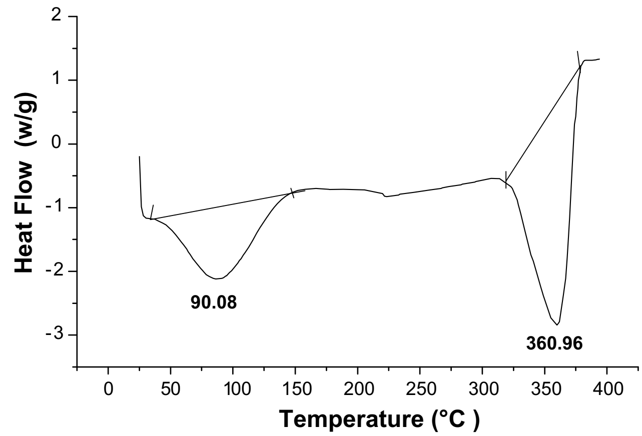


Fig. 3. DSC plot of the unmodified cellulose.

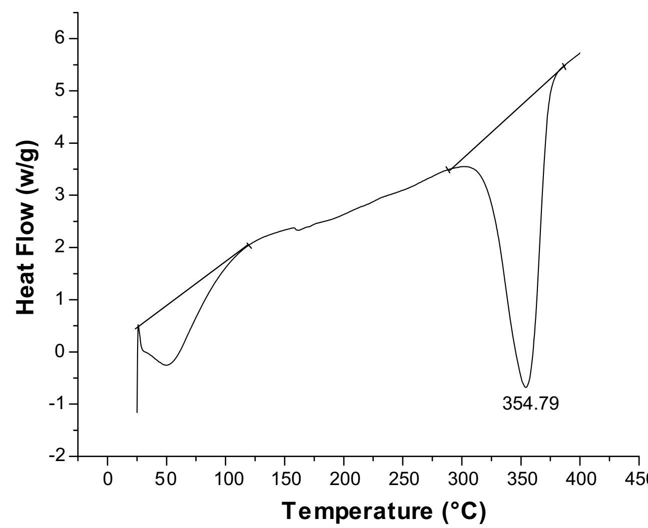


Fig. 4. DSC plot of the novel cellulose.

Table 2
Physics property of novel antibacterial cellulose

Samples	Tensile strength (N)	Elongation at break (mm)	Tearing strength (N)	WRA (°,w + f)
Untreated	385.1	25.531	16.02	209.4
Modified	378.3	21.845	15.68	211.3

Table 3
Antibacterial properties of the novel cellulose materials

Samples (washing cycle)	*R* (%, *S. aureus*)
0	99.68
1	98.43
5	96.83
10	91.14
20	84.07

cellulose against *S. aureus* were evaluated by ASTM E2149-01. The test method was designed to evaluate the resistance of non-leaching antimicrobial treated specimens to the growth of microbes under dynamic contact conditions. Washing cycles were tested according domestic machine standard. The antibacterial activities of the cellulose fabric containing the multi-cationic groups are summarized in Table 3. It can be seen that antibacterial properties of the novel cellulose materials were excellent. The reduction of modified cellulose reached 84.07% after washed 20 times. It demonstrates that the incorporation of multi-cationic and benzyl groups may improve antibacterial activity. It will have potential application in some field.

4. Conclusions

Cellulose fabric was chemically modified with the triazine derivatives containing the multi-cationic benzyl groups. The modified cellulose showed a significant change of chemical structure and surface properties. The nitrogen content of the modified cellulose significantly increased. The thermal stability of the modified cellulose was slightly decreased. Physical properties of the novel antibacterial cellulose had not significant change. The novel antibacterial cellulose was imparted excellent antibacterial properties. The reduction of the modified cellulose reached 84% after washed 20 times. The incorporation of multi-cationic and benzyl groups could improve antibacterial activity.

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