

# Chemical and morphological structures of modified novel cellulose with triazine derivatives containing cationic and anionic groups

Kongliang Xie <sup>a,\*</sup>, Aiqin Hou <sup>b</sup>, Yan Sun <sup>a</sup>

<sup>a</sup> Modern Textile Institute, Donghua University, Shanghai 200051, PR China

<sup>b</sup> National Engineering Research Center for Dyeing and Finishing of Textiles, Donghua University, Shanghai 200051, PR China

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## Abstract

Cellulose fabric was chemically modified with the compounds containing cationic and anionic groups. The molecular chains of modified cellulose had both cationic and anionic groups. The chemical and morphological structures of modified cellulose were investigated with X-ray diffraction, FTIR spectra, differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and nitrogen content analysis. The crystallinity and preferred orientation of novel cellulose decreased. The thermal stability of the modified cellulose was slightly improved. Representative scanning electron micrographs indicated there appears to be appreciable difference in the appearance of the surfaces of the unmodified and the modified cellulose fibers.

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**Keywords:** Modification; Cellulose; Morphological structures; Chemical structures

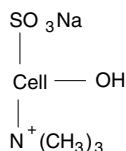
## 1. Introduction

Many properties of materials are dependent on the surface structure and chemical modification. The cellulose fiber is one of the excellent natural materials that have wide application in the different production. Besides the traditional use as textile materials, cellulose has been 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, 2001; Kulpinski, 2005; Lee & Kim, 2001; Lou, Zhang, & Chen, 2003). Chemical modification of cellulose can change itself chemical and morphological structures for different propose. A number of attempts have been made to modify the cellulose fiber using the compounds containing the certain groups. For example, cellulose to which cross-linking has been introduced has improved elastic recovery due to the inhibition of slippage between the molecules when forces are applied (Jiang, Meng, & Qing, 2006; Sch-

ramm, Bischof, & Katovic, 2002; Xie, Hou, & Zhang, 2006). In our recent research work, net modified cellulose fabric with a 1,3,5-triazine derivative containing the multi reactive groups was investigated (Xie, Sun, & Hou, 2006). However, molecular chains of modified cellulose fabric with Tri-HTAC only have cationic groups. Its application and product processing in the composite materials field can be limited. The surface properties of cellulose are crucial important in many applications, due to their strong influence on wetting, coating and adhesion characteristics of the materials. Cellulose fabric was chemically modified with compounds containing cationic and anionic groups. The molecular chains of modified cellulose have both cationic and anionic groups (For example, Scheme 1). They form new structure like silk protein and change the surface chemical structure and property of cellulose.

The modified cellulose with compounds containing cationic and anionic groups can get the cationic and anionic surface charge, simultaneously. The reports of modified cellulose with compounds containing cationic and anionic groups are scarce. In this paper, the compounds containing cationic and anionic compounds are applied to modify

\* Corresponding author. Tel.: +86 21 6237 8237; fax: +86 21 6237 8392.  
E-mail address: [klxie@dhu.edu.cn](mailto:klxie@dhu.edu.cn) (K. Xie).



Scheme 1.

cellulose. The composition (Tri-HTAC-Bi-CSAT) are consisted of a 1,3,5-triazine derivative containing the reactive groups, 2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC) and 2,4-bichloro[(6-sulfanilic acid anhydrous)-1,3,5-triazine] (Bi-CSA). The chemical and morphological structures of the modified cellulose are investigated with X-ray diffraction (XRD), FT-IR spectra, differential scanning calorimetry (DSC), scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Materials

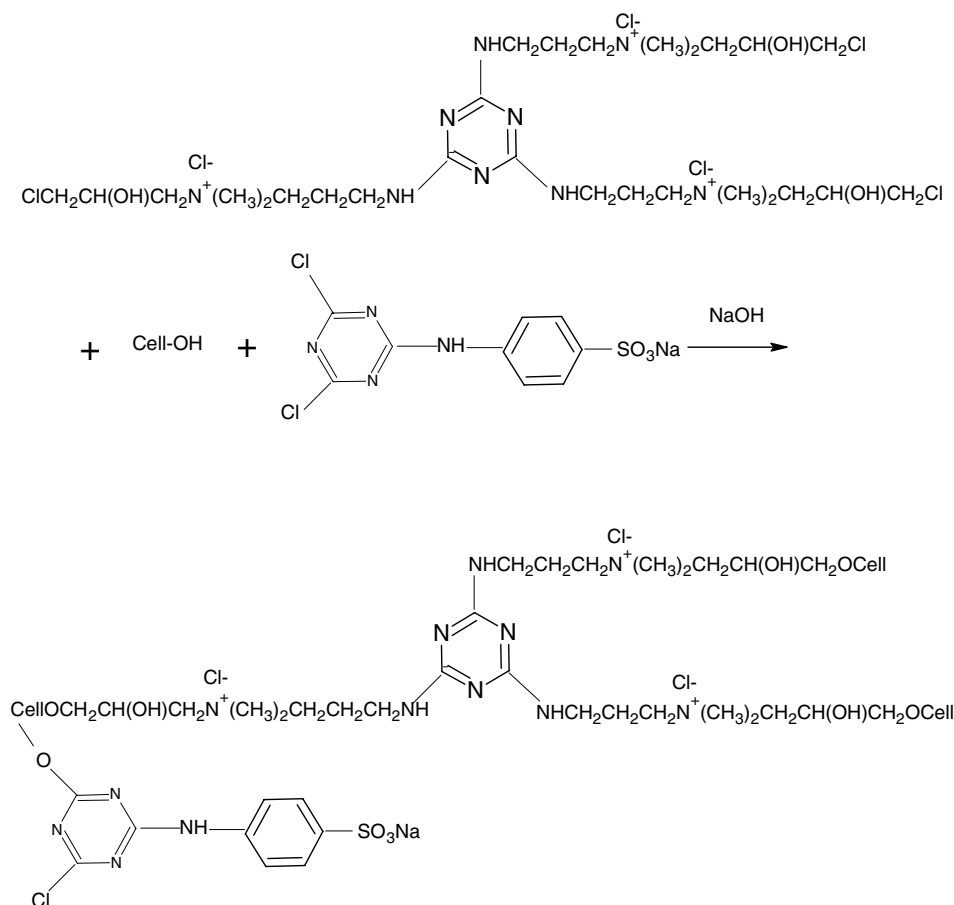
Desized, scoured and bleached cellulose fabrics were obtained from Beijing Textile Company. The 1,3,5-triazine derivative containing the reactive groups, 2,4,6-tri[(2-

hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC) and 2,4-bichloro[(6-sulfanilic acid anhydrous)-1,3,5-triazine] (Bi-CSAT) were obtained from National Engineering Research Center for Dyeing and Finishing of Textiles (Shanghai).

### 2.2. Modification to cellulose fabric with the composition

The 1,3,5-triazine derivative containing the reactive groups, 2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC) was dissolved in distilled water to give the certain concentration solution. 2,4-Bichloro[(6-sulfanilic acid anhydrous)-1,3,5-triazine] (Bi-CSAT) was added in the Tri-HTAC solution to give the certain quantity solution (Tri-HTAC:Bi-CSAT = 5:1 w/w).

Tri-HTAC-Bi-CSAT solution was diluted in distilled water to give 8% solution by weight. To the solution was added 1.5% sodium hydroxide as catalyst. Samples of cellulose were treated with the solutions in the dyeing machine (PYROTEC-2000). The samples were kept at room temperature for 4 h. The treated fabrics were then washed with tap water until neutral and soaped in a solution of a non-ionic surfactant (OP-10, 1 g/l) at 60 °C for 30 min at liquor ratio 1:100 using a domestic washing machine to remove



Scheme 2.

unfixed compounds. The fabrics were removed, rinsed thoroughly in hot tap water until the rinsing water was clear. The fabrics were dried at ambient conditions.

### 2.3. XRD

The modified cellulose and unmodified cellulose samples were cut into powder. The X-ray diffraction patterns of the fabrics were measured with a D/max-2550 PC X-ray Diffractometer (Rigaku Corporation, Japan), which used Cu–K target at 40 kV 300 mA,  $\lambda = 1.542 \text{ \AA}$ .

### 2.4. FT-IR spectra

The IR was recorded on a Nexus-670 (Nicolet Co.).

### 2.5. Nitrogen content

The percentage nitrogen content was determined by Elementar Vario(III) (Germany). The samples were dried under vacuum at the temperature of  $50^\circ\text{C}$  before measuring.

### 2.6. 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  $400^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C}/\text{min}$ , under a constant flow of dry nitrogen.

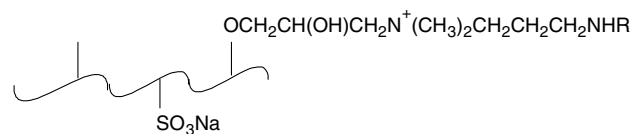
### 2.7. SEM

For SEM analysis, the fabric materials were sputtered with gold and then examined with a JSM 5600LV scanning electron microscope (JEOL, Tokyo, Japan), operated at 15 kV.

## 3. Results and discussion

### 3.1. The chemical structures of novel cellulose

The molecular structure of cellulose has a lot of hydroxyl. The compounds (Tri-HTAC–Bi-CSAT) were able to form covalent bonds with cellulose under alkaline conditions (Scheme 2). The modified cellulose fibers formed new molecular structures containing not only cationic but also anionic groups (Scheme 3). IR spectra of unmodified and modified cellulose are shown in Figs. 1 and 2, respectively. FT-IR spectra of modified cellulose assured the presence of  $\text{N}=\text{C}$  at  $1595 \text{ cm}^{-1}$  (1,3,5-triazine cycle). The nitrogen contents of unmodified and modified cellulose were determined (shown in Table 1). Compared with unmodified cellulose, the nitrogen contents of modified cellulose increased. This confirms that the compounds (Tri-HTAC–Bi-CSAT) were able to form covalent bonds with cellulose.



Scheme 3.

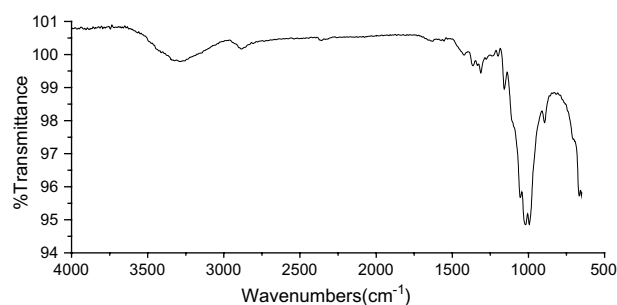


Fig. 1. FT-IR spectrum of unmodified cellulose.

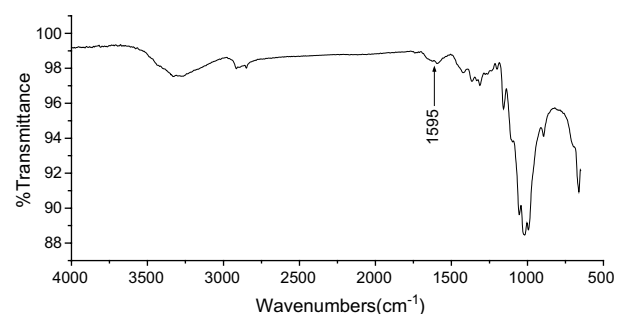


Fig. 2. FT-IR spectrum of modified cellulose.

Table 1  
Analysis nitrogen content

	Unmodified cellulose	Modified cellulose
N (%)	0.346	0.441

### 3.2. Morphological changes of novel cellulose

After cellulose was modified with Tri-HTAC–Bi-CSAT, the morphological structure may be changed. The X-ray diffraction analyses of unmodified and modified cellulose were carried out. The curves of the crystallinity of unmodified and modified cellulose are shown in Figs. 3 and 4, respectively. The X-ray diffraction analyses of them are listed in Table 2. The curves of the preferred orientation (P.O.) of unmodified and modified cellulose are shown in Figs. 5–10. The crystallinities and P.O. were calculated, respectively. The results are listed in Table 3.

Table 3 shows that the crystallinity and P.O. of modified cellulose were slightly decreased. Dry crease recovery angles (CRA) were measured by a P500570 (SDL) according to AATCC Test Method 66-2003. Dry crease recovery

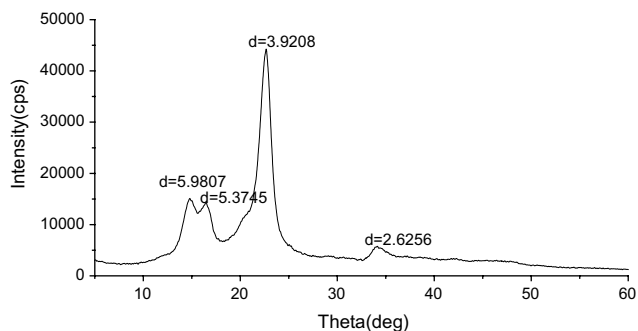


Fig. 3. The X-ray powder diffraction profile of unmodified cellulose.

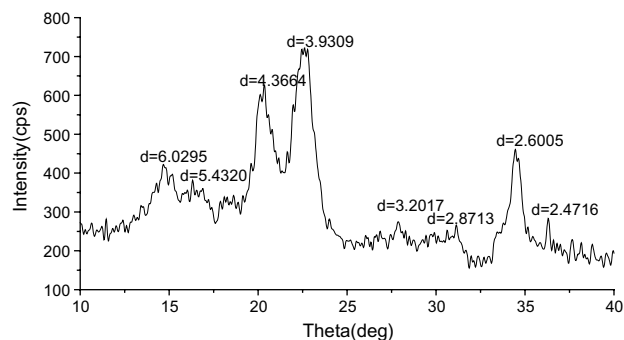


Fig. 6. The X-ray powder diffraction profile of unmodified cellulose (90°).

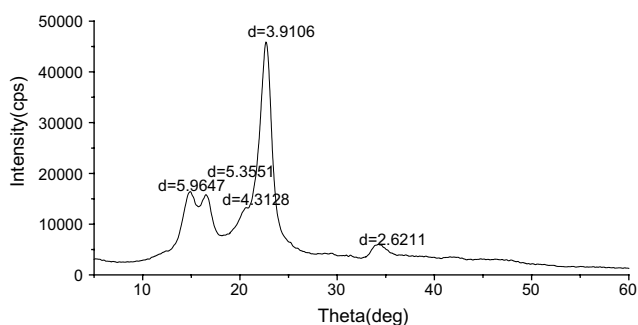


Fig. 4. The X-ray powder diffraction profile of novel cellulose.

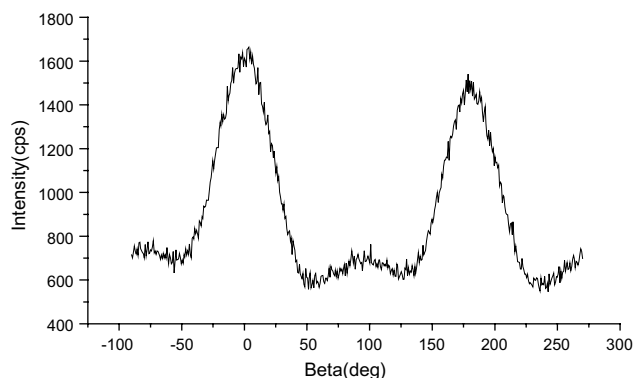


Fig. 7. The X-ray powder diffraction profile of unmodified cellulose (360°).

Table 2  
Data of X-ray diffraction peaks of unmodified and novel cellulose

Material	2θ (°)	Half-peak breadth (Å)	Spacing d (Å)
Unmodified cellulose	14.800	0.789	5.9807
	16.480	0.736	5.3745
	22.660	0.827	3.9208
	34.121	0.779	2.6256
Novel cellulose	14.840	0.827	5.9647
	16.540	0.703	5.3551
	22.720	0.840	3.9106
	34.181	0.913	2.6211

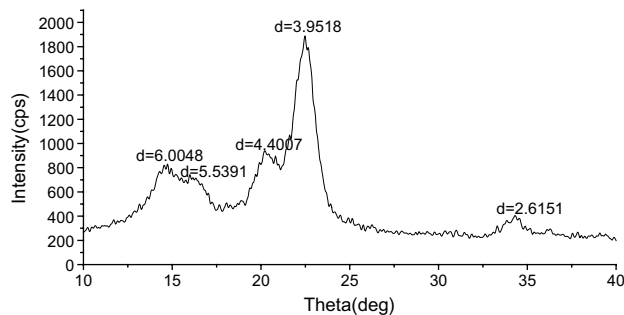


Fig. 8. The X-ray powder diffraction profile of novel cellulose (0°).

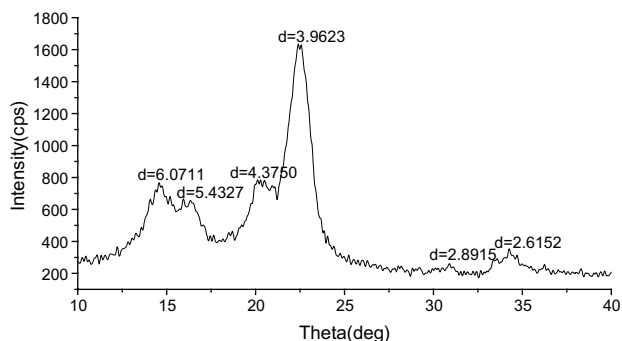


Fig. 5. The X-ray powder diffraction profile of unmodified cellulose (0°).

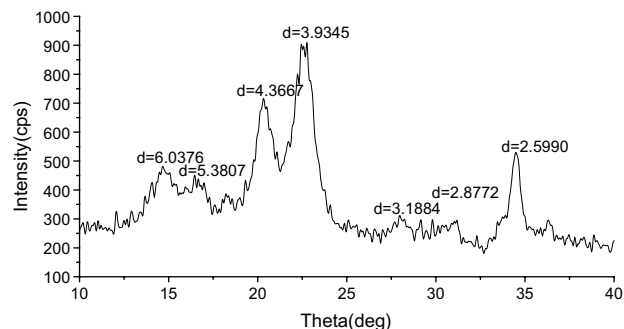


Fig. 9. The X-ray powder diffraction profile of novel cellulose (90°).

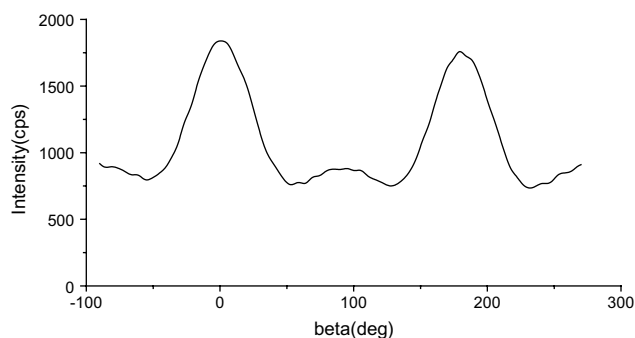


Fig. 10. The X-ray powder diffraction profile of novel cellulose (360°).

Table 3  
Crystallinity and P.O. of unmodified and novel cellulose

Sample	Crystallinity (%)	P.O. (%)
Unmodified cellulose	62.61	71.1
Modified cellulose	61.96	70.8

angles [(W+F)] of modified and unmodified cotton were 162°, 128°, respectively. It shows that the crease recovery angle (CRA) of modified noticeably increased. The change of physical properties is mainly due to crosslinking reaction occurred in the more accessible amorphous regions of cotton.

### 3.3. Thermal properties of novel cellulose

Differential scanning calorimetry (DSC) is one of important methods for observing the thermal characteristics of materials. After cellulose fabric was chemically modified with Tri-HTAC–Bi-CSAT composition, the chemical and morphological structures of the modified cellulose would change. The chemical modification had an effect upon the thermal stability of modified cellulose. Figs. 11 and 12 show the DSC plots of the unmodified and modified cellulose with Tri-HTAC–Bi-CSAT, respectively. For the unmodified cellulose, the endothermic peak initiated at 322.23 °C, finished at 376.88 °C. For the modified cellulose, the endothermic peak initiated at 329.11 °C, finished at 377.99 °C. Moreover, the modified cellulose exhibited major endothermic peak at 362.53 °C. The position of the

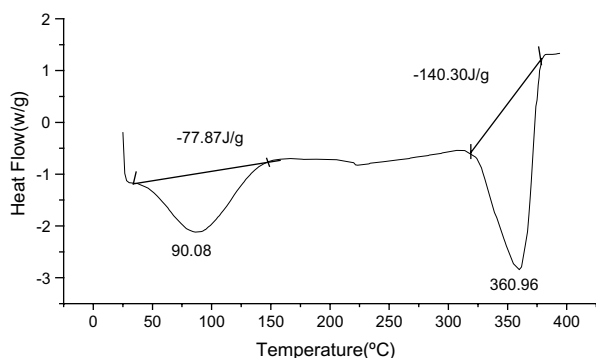


Fig. 11. DSC plots of unmodified cellulose.

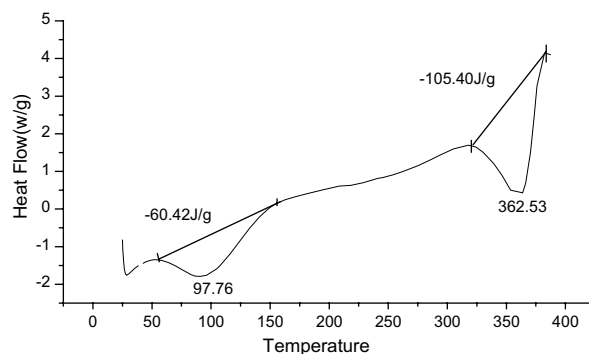


Fig. 12. DSC plots of novel cellulose.

above endothermic peak was more than 1.5 °C higher than 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 fabric 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 improved.

The DSC plot for unmodified and modified cellulose fabric also contained endothermic peaks at temperatures of 90.08 and 97.76 °C, respectively. The peak area of the endothermic peak in the DSC plot for unmodified cellulose was greater than that obtained in the DSC plot for modified cellulose. These endothermic peaks are probably associated with the removal of water from the cellulose polymer chains. The lower peak area obtained in the DSC plot of modified cellulose is probably due to a decrease in the physical in the amount of water trapped within the polymer chains, which is brought about by changes in the physical and hydrophobic (1,3,5-triazine) of the cellulose after modified.

### 3.4. Surface morphological of modified fabric

SEM analysis was used to characterize any changes about the surface morphology of the cellulose. Representative SEM micrographs, taken at the magnification of 3000 of unmodified and modified cellulose fibers with

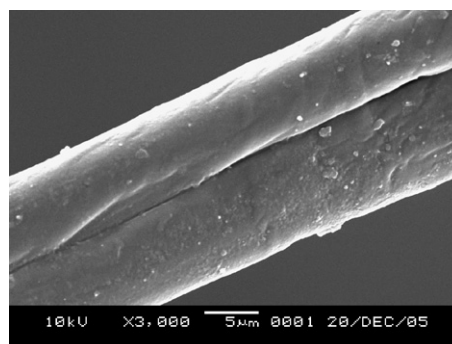


Fig. 13. SEM micrograph of unmodified cellulose fibers.

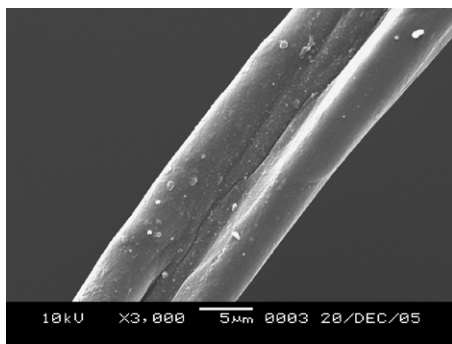


Fig. 14. SEM micrograph of the novel cellulose fibers.

Tri-HTAC–Bi-CSAT compounds were shown in Figs. 13 and 14. From Figs. 13 and 14, it can be seen that there were slight pitting and cracking or crazing on the surface of unmodified cellulose. However, the surface of modified cellulose was smooth. The morphological changes of cellulose fibers may be swelled in the solution of 1.5% sodium hydroxide as catalyst in the crosslinking reaction process.

#### 4. Conclusions

Cellulose fabrics were modified with Tri-HTAC–Bi-CSAT compounds. Modified cellulose showed a significant change of chemical structure and physical morphology. The crystallinity and P.O. of modified cellulose slightly decreased. The nitrogen contents of the

modified cellulose increased. The thermal properties and surface morphological of modified cellulose showed significant change. The thermal stability of the modified cellulose slightly improved. SEM micrographs indicate that cellulose fibers swelled during modification.

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