The Morphological Structures of Net-Modified Cotton Cellulose with Triazine Derivative Containing Multireactive Groups

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Received 25 January 2006; accepted 24 March 2006
DOI 10.1002/app.24476
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Cotton fabric was chemically modified with a 1,3,5-triazine derivative containing multireactive and multicationic groups, 2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC). The morphological structures of net-modified cotton cellulose were investigated with differential scanning calorimetry, X-ray diffraction, and scanning electron microscopy. The results showed that crystallinity and preferred orientation of net-modified cellulose decreased. The tensile strength of net-modified cotton decreased and crease recovery angle increased. The thermal stability of the net-modified cotton was slightly improved. Representative scanning electron micrographs indicated that there appears to be appreciable difference in the appearance of the surfaces of the unmodified and the net-modified cotton fibers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2700–2707, 2006

Key words: reactive quaternary agent; modification; salt-free dyeing; synthesis

INTRODUCTION

The cellulose fibers dye systems pose environmental questions because of their current high salt requirement and colored effluent discharge. Since cotton adopts an anionic surface charge in water, these dyes have low intrinsic affinity for the cellulose fiber. The repulsive charge between dye and cotton can be overcome by adding an electrolyte such as sodium sulfate, which has the effect of screaming the surface charge on the cellulose fiber. To reduce the usage of salt and increase dye-bath exhaustion, a number of attempts have been made to modify the cotton fiber, using the compounds containing the certain groups. The cationic cotton, which has been chemically modified with Glytac A or epichlorohydrin derivatives, has been thoroughly investigated.[1–5] These were mainly compounds containing mono- and bi-reactive group, but unfortunately many of the chemicals used were not resistant to hydrolysis. Recently, we investigated net-modified cotton fabric with a 1,3,5-triazine derivative containing the multireactive and multicationic groups, 2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC). Compared with unmodified cellulose, the net-modified cotton cellulose exhibits different behavior towards dyeing. The color yield was higher than that on untreated cotton, despite the addition of large amounts of salt in the latter case. After dyeing, the reflectance spectra of modified cotton did not change, when compared with that of unmodified cellulose with reactive dyes. The modified cotton got better wash fastness than the untreated cotton. This will be of great benefit, as it will enable a reduction in the salt present in the dye-house effluent.

Tri-HTAC was able to form covalent bonds with fibers under alkaline conditions (Scheme 1).

After the cotton fabric was treated with a 1,3,5-triazine derivative containing the multireactive and multicationic groups, the morphological structure of the net-modified cotton cellulose maybe changed. In this paper, triazine derivative containing the multireactive and multicationic groups (Tri-HTAC) was applied to modify cotton cellulose. The morphological structures of net-modified cotton cellulose were investigated with X-ray diffraction (XRD) and scanning electron microscopy (SEM). The thermal stability and physical properties of net-modified cotton cellulose was examined using differential scanning calorimetry (DSC).

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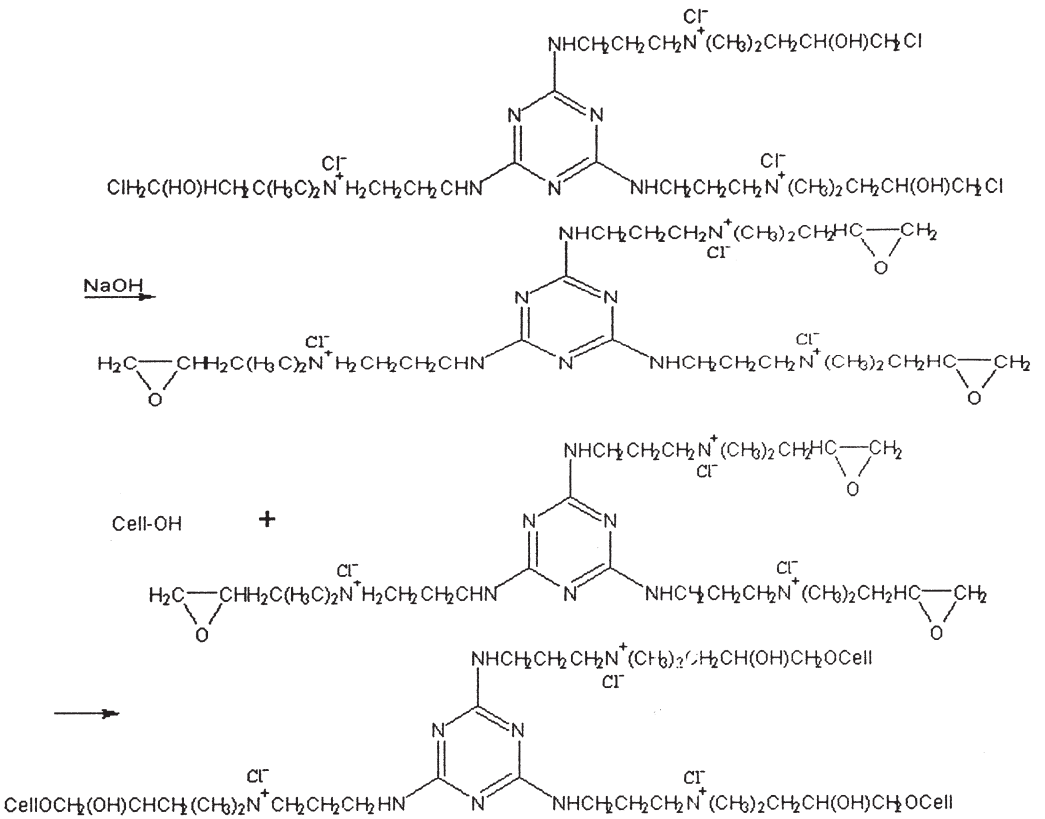

Scheme 1

EXPERIMENTAL

Materials

Desized, scoured, and bleached cotton fabrics were obtained from Beijing Textile Company.

Net modification of cotton fabric

2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC) was dissolved in distilled water to give solutions at 10% concentration by weight. Sodium hydroxide (1.5%) was added as catalyst to the solution. Samples of cotton were padded with the solutions to give 100% wet pick-up, were placed in plastic sample bags and were tightly sealed to prevent air penetration. The samples were kept at room temperature for 4 h. The treated fabrics were then washed with tap water until neutral and were again washed in warm water, using a domestic washing machine to remove un-

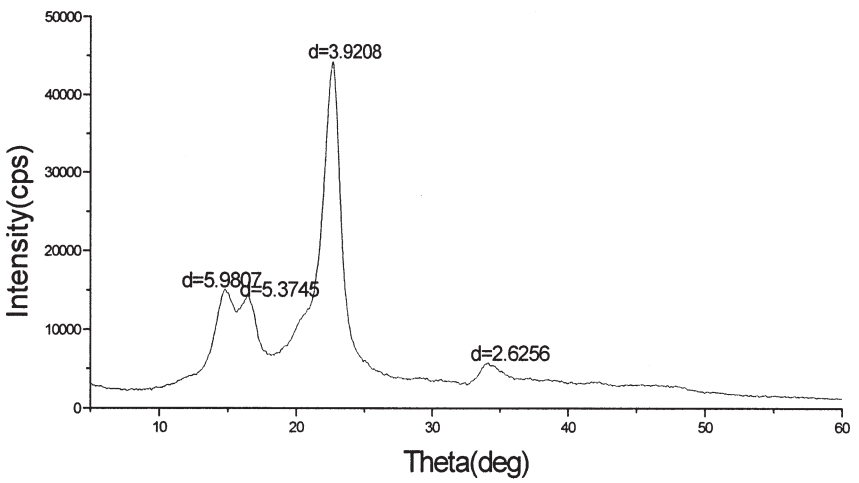

Figure 1 The X-ray powder diffraction profile of unmodified cotton.

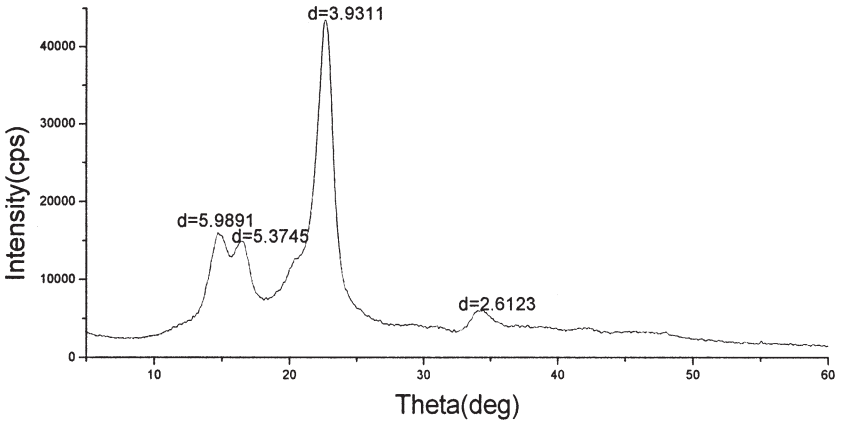

Figure 2 The X-ray powder diffraction profile of net-modified cotton.

fixed Tri-HTAC. The fabric was air-dried at room temperature.

X-ray diffraction

The net-modified cotton and unmodified cotton samples were cut into powder. The X-ray diffraction (XRD) patterns of the fabrics were measured with a D/max-2550 PC X-ray diffractometer (Rigaku, Japan), which used Cu K target at 40 kV 300 mA, $\lambda = 1.542$ E.

Differential scanning calorimetry

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°C, at a scanning rate of 10°C/min, under a constant flow of dry nitrogen.

Scanning electron microscopy

For scanning electron microscopy (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.

Nitrogen content

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

Physical property measurements

Fabric tensile strength was determined by using a H10KS tensile testing machine (Hounsfield SDL). Six specimens (three for warp and three for weft) were

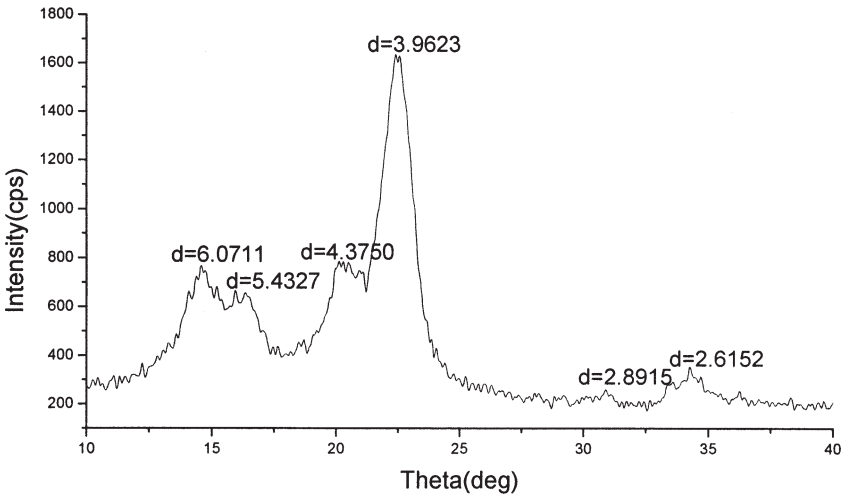

Figure 3 The X-ray powder diffraction profile of unmodified cotton (0°).

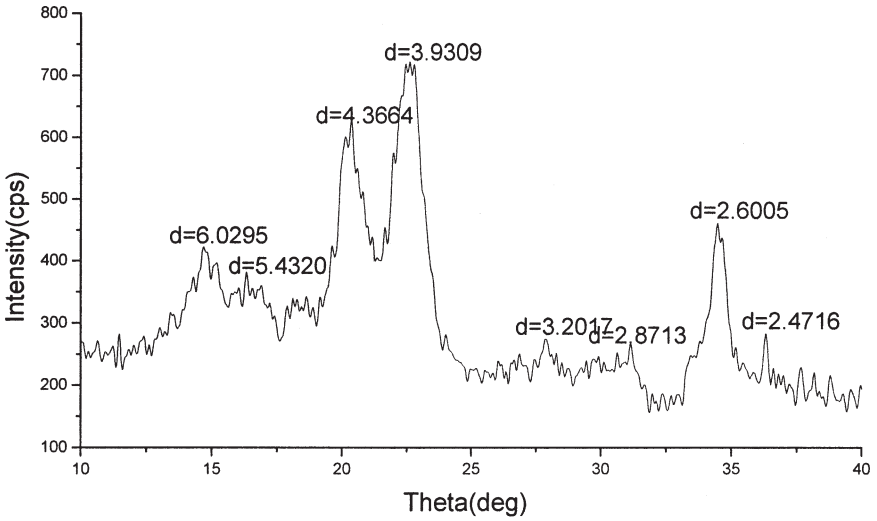

Figure 4 The X-ray powder diffraction profile of unmodified cotton (90°).

tested at a gauge length of 200 mm with a stain rate of 30 mm/min. The width of the specimen was 50 mm.

Dry crease recovery angles (CRA) were measured by using a P500570 (SDL) according to AATCC Test Method 66–2003.

RESULTS AND DISCUSSION

Morphological changes of net-modified cotton fabric

Cotton fabric was treated with a 1,3,5-triazine derivative containing the multireactive and multicationic groups. Compared with unmodified cellulose, the net-modified cotton cellulose showed different behavior towards dyeing. The morphological structure of the net-modified cotton cellulose maybe changed. Because the triazine derivative could form net crosslinking with cellulose, there are many covalent bonds in modified cellulose molecules containing a lot of cationic groups. XRD analyses of cotton and net-modified cotton cellulose were carried out. The curves of the crystallinity of unmodified and net-modified cotton are shown in Figure 1 and Figure 2, respectively. The curves of the preferred orientation (PO) of unmodified and net-modified cotton are shown in Figures 3–8. The XRD analyses of unmodified and net-modified cotton are listed in Table I. The crystallinities and PO were calculated, respectively. The results are shown in Table II.

Table II shows that the crystallinity and PO of net-modified cellulose was slightly decreased. The nitrogen contents of unmodified and net-modified cotton were determined (shown in Table II). Compared with that of unmodified cotton, the nitrogen content of net-modified cotton increased. This confirms that Tri-HTAC was able to form covalent

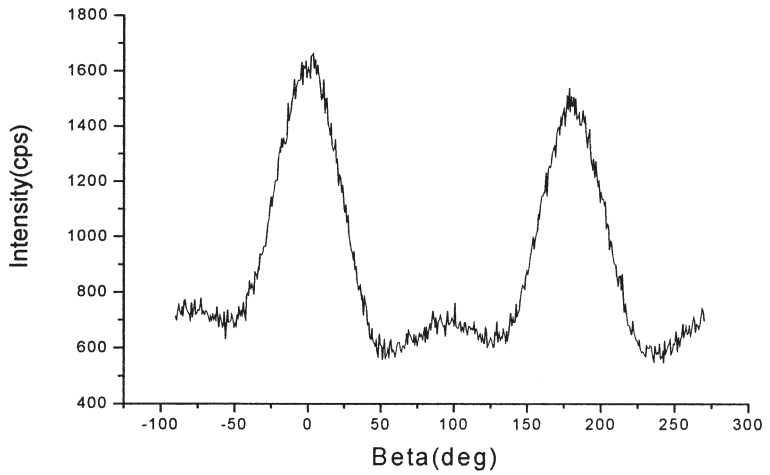

Figure 5 The X-ray powder diffraction profile of unmodified cotton (360°).

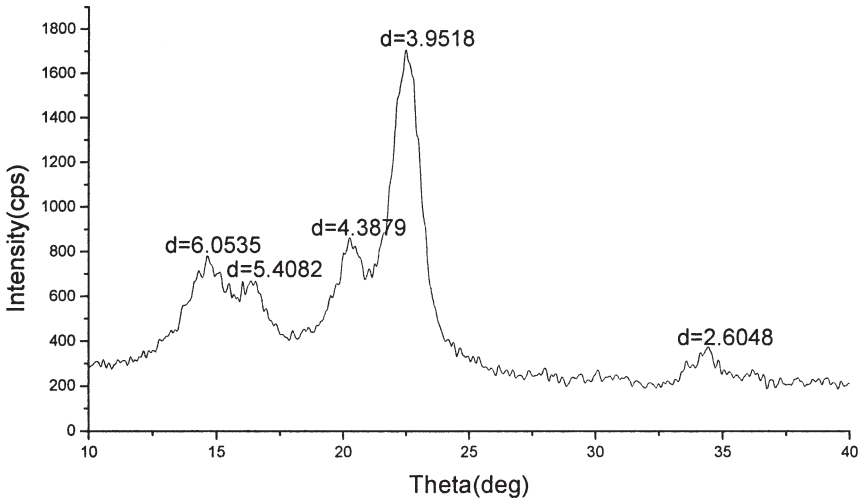

Figure 6 The X-ray powder diffraction profile of net-modified cotton (0°).

bonds with fibers. The dyeing properties of the net-modified cotton were markedly affected because of the formation of ionic bonds and the change of morphological structure.

Physical properties of the net-modified cotton

Physical properties of the modified cotton may also be changed. The tensile strength and CRA of net-modified and unmodified cotton are shown in Table III. Table III shows that net-modified cotton fabric did exhibit a substantial improvement of dry resiliency. In addition, the net-modified cotton fabric showed a slight decrease in tensile strength. These changes of physical properties are mainly due to the net crosslinking reaction that occurred in the more accessible amorphous regions of cotton.

Thermal properties of net-modified cotton fabric

Figures 9 and 10 show the DSC plots of unmodified and net-modified cotton, respectively. For the unmodified cotton, the endothermic peak initiated at 322.23°C, finished at 376.88°C. For the net-modified cotton, the endothermic peak initiated at 325.64°C, finished at 379.40°C. Moreover, the net-modified cotton exhibited major endothermic peak at 365.34°C.The position of the above endothermic peak was more than 4°C higher than that of unmodified cotton. The endothermic changes obtained in the DSC plot for cotton are associated with decomposition processes, which may occur within the fabric during heating. The endothermic peaks occurring in the DSC plots for both untreated and net-modified cotton fabric are possibly due to either

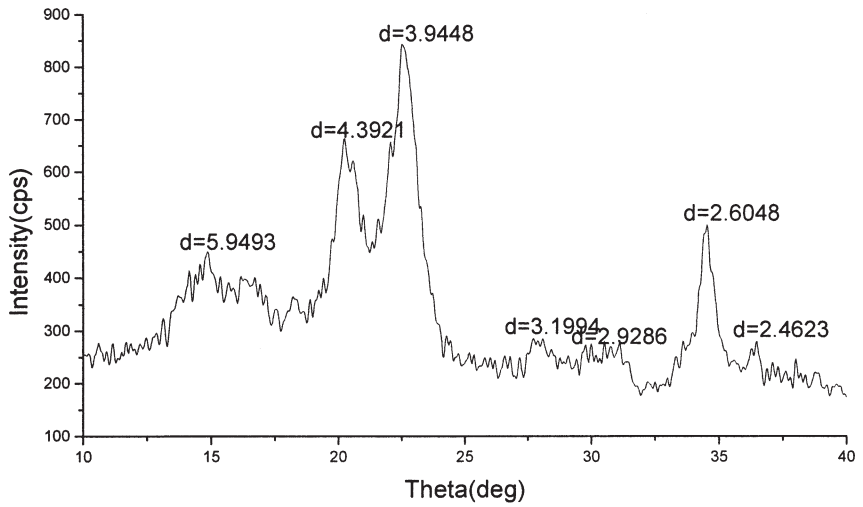

Figure 7 The X-ray powder diffraction profile of net-modified cotton (90°).

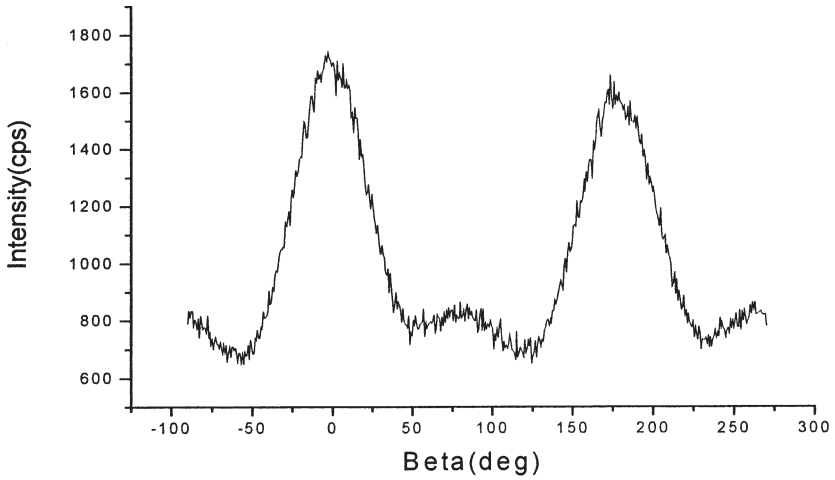

Figure 8 The X-ray powder diffraction profile of net-modified cotton (360°).

local changes in the crystalline regions of natural cotton or a breakdown in the net-modified cotton on heating. This phenomenon showed that the thermal stability of the net-modified cotton improved slightly.

The DSC plot for untreated cotton and net-modified cotton fabric also contained endothermic peaks at temperatures of 90.08 and 95.90, respectively. The peak area of the endothermic peak in the DSC plot for untreated cotton was greater than that obtained in the DSC plot for net-modified cotton. 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 net-modified cotton 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) properties of the polymer after net modified.

TABLE I
Dates of X-ray Diffraction Peaks of Unmodified and Net Modified Cotton

Samples	2θ (°)	Half-peak breadth (Å)	Spacing *d* (Å)
Unmodified cotton	14.800	0.789	5.9807
	16.480	0.736	5.3745
	22.660	0.827	3.9208
	34.121	0.779	2.6256
Net modified cotton	14.779	0.834	5.9891
	16.480	0.762	5.3745
	22.600	0.863	3.9311
	34.299	1.067	6.2123

TABLE II
Crystallinity, P.O, and Nitrogen Content of Unmodified and Net Modified Cotton

Samples	Nitrogen content (%)	Crystallinity (%)	P.O (%)
Unmodified cotton	0.346	62.61	71.1
Net modified cotton	0.411	60.93	70.3

Surface morphology of fabric

SEM analysis was used to characterize any changes in the surface morphology of the fibers. Representative SEM micrographs, taken at the magnification of 8000 of unmodified and net-modified cotton fibers are shown in Figures 11 and 12. From Figure 11 and 12, it can be seen that there was slight pitting and cracking or crazing on the surface of unmodified cotton. However, the surface of net-modified cotton was smooth. The morphological changes were mainly because cotton fibers swelled in the net crosslinking reaction process.

CONCLUSIONS

It is concluded that the net-modified cotton cellulose showed a rather significant change of physical morphology. Compared with that of unmodified cellulose, the crystallinity and PO of net-modified cellulose slightly decreased. The nitrogen contents of the

TABLE III
Tensile Strength and Crease Recovery Angle of Net Modified and Unmodified Cotton

Samples	Tensile strength ($N/5 \times 20$ cm) Warp	Weft	Dry crease recovery angle [$(W + F)$](°)
Unmodified cotton	667.56	312.76	128
Net modified cotton	611.87	305.2	154

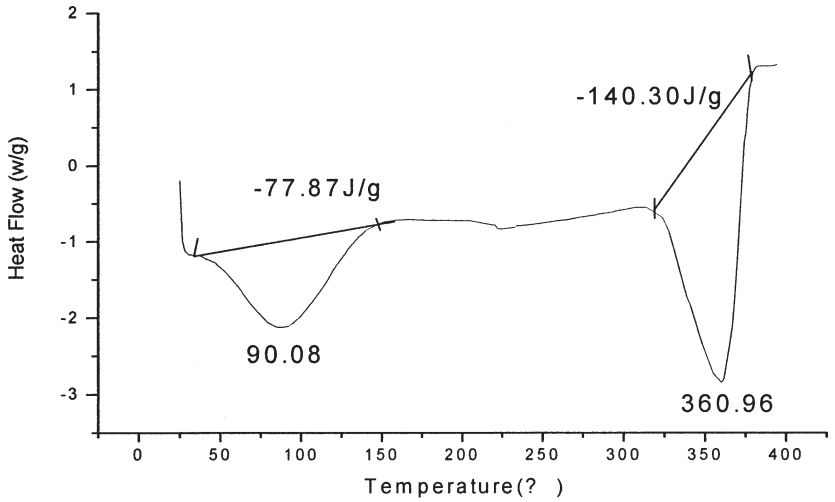

Figure 9 DSC plots of unmodified cotton.

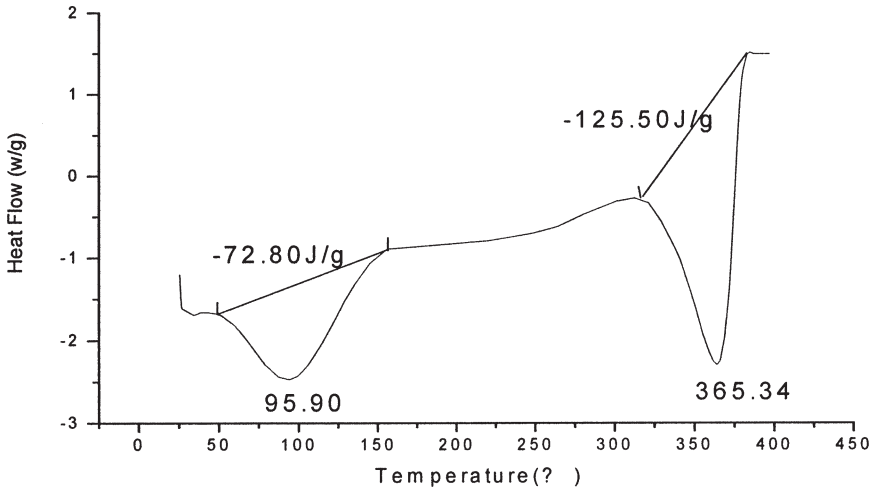

Figure 10 DSC plots of net-modified cotton.

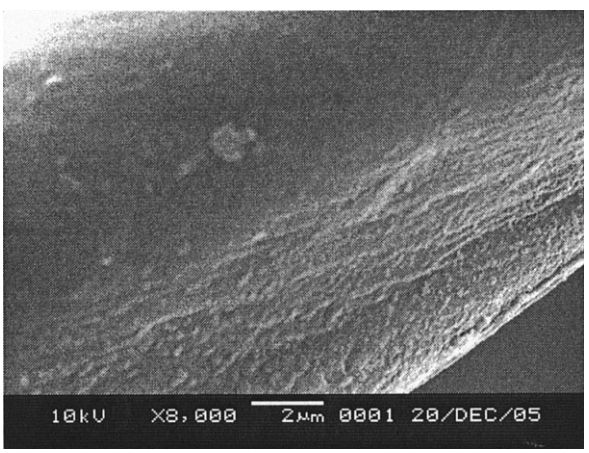

Figure 11 SEM micrographs of unmodified cotton fibers.

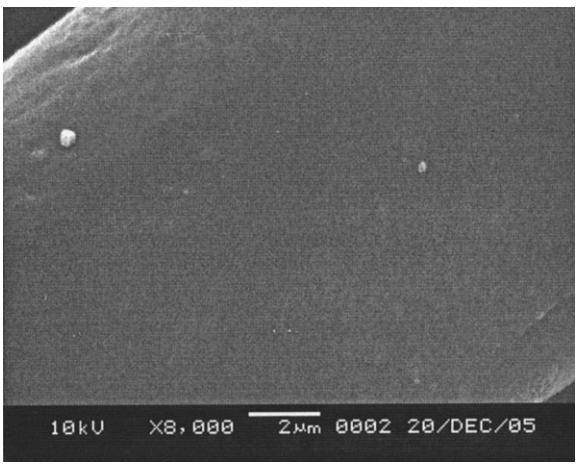

Figure 12 SEM micrographs of net-modified cotton fibers.

net-modified cotton increased. The tensile strength of net-modified cotton decreased and CRA increased. The thermal stability of the net-modified cotton slightly improved. This confirms that Tri-HTAC was able to form covalent bonds with fibers. Representative SEM micrographs indicated that cotton fibers swelled during modification.

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