

Effect of Solvents on Cyanoethylation of Cotton Cellulose and Its Properties

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ABSTRACT: The cyanoethylation of cotton fabric was carried out using aqueous sodium hydroxide with acrylonitrile in presence of solvents like acetone and ethanol in different concentrations. The modified cellulose was investigated with vertical wicking test, X-ray diffraction (XRD), thermogravimetry-differential thermal analysis (TG/DTA), and atomic force microscopy (AFM). The wicking height was increased for the modified cellulose. Modified cellulose had increase in crystallinity index

with reduction of crystallite size. The thermal stability of the modified cellulose was also increased. The images produced using AFM technique revealed that there is appreciable difference in the surface roughness between scoured, mercerized, cyanoethylated and solvent treated samples. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1622–1627, 2011

Key words: modification; swelling; XRD; TG/DTA; AFM

INTRODUCTION

Cellulose is the most abundant natural polymer on earth, consisting of glucose–glucose linkages arranged in linear chains.¹ It has a strong interaction with water by forming stable bridges through intermolecular hydrogen bonds. In presence of excess of water, hydrated polymers may swell and exhibit changes in mechanical and chemical properties.² Water molecules, when diffuse into the amorphous region, can break intermolecular hydrogen bonds among cellulose chains and increasing their intermolecular distance.³

Since water penetrates the amorphous regions of cellulose fibers, the concept of water absorption is closely related with crystallinity. In nature, cellulose microfibrils in cotton fiber walls are highly crystalline with a crystallinity index of 70–80%. By impregnation of cotton fiber with alkaline swelling agents and by reacting with some chemical agents that can be substituted for hydroxyl groups of cellulose molecules present in the amorphous region, a (highly accessible or decrystallized) cotton fibers can be obtained.⁴ If the amorphous domains of cellulose are attacked, chain scission and peeling reactions occur, which reduce the total amount of amorphous cellulose and therefore increase the relative degree of crystallinity. At the same time, there is also the possibility that random cleavage of the cellulose occurs

in the accessible chains within the crystalline domains.⁵ The chains at the outer portions of the crystallites can cleave randomly and protrude from the crystalline domain.⁶

For improved hydrophilicity, better adsorption capacity, bioactive properties, etc., industries depend on chemical modification process. One of the substitution reactions, cyanoethylation, is achieved by the permanent attachment of chemical groups to the basic unit of fiber structure forming cyanoethyl cellulose. An extensive research^{7–15} had been done for imparting cellulose fabrics with new properties like resistance to heat, organic acids, and microorganisms.

Recently the $-\text{C}\equiv\text{N}$ group present in the cyanoethyl cellulose of alkaline scoured cotton fabric was hydrolyzed to get $-\text{CONH}_2$ group by acetone and ethanol-induced hydroxylation in the presence of alkali and reported that an increased IR index, crease recovery, and dye uptake with reactive dye.^{16,17} There is no report on the water absorption, crystallinity index, thermal properties, and surface roughness of cotton fabric after chemical modification with acrylonitrile/acetone and acrylonitrile/ethanol mixture. Hence, the present work aims to characterize the modified cellulose by vertical wicking test, XRD, TG/DTA, and AFM techniques.

EXPERIMENTAL

Materials

Plain weave 100% cotton fabric (Ends/in.: 140; Picks/in.: 80, Count: 40 s, Weight/sq cm—0.015 g) was used throughout the study. All the chemicals used,

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were laboratory grade. Deionized water was used throughout the study.

Chemical modification

The scoured cotton fabric was kept immersed in aqueous sodium hydroxide (18% w/w) solution for about 30 min at room temperature, squeezed well, and then treated with acetone/acrylonitrile reaction mixture for about 30 min at room temperature. Then the fabric was squeezed well, washed, neutralized with acetic acid, washed again, and air-dried. The reaction mixture ratio starts with acetone (2 mL)/acrylonitrile (8 mL) and further ratios are taken with increasing/decreasing 2 mL each of the respective components until it reaches to the ratio of acetone (10 mL)/acrylonitrile (0 mL). The samples were designated as AE - X, where AE = acetone and X = 2–10 mL. The same method was repeated by replacing the acetone with ethanol in the above reaction mixture and the samples were designated as EL - X where EL = ethanol, and X = 2–10 mL. The control sample was prepared with 10 mL of acrylonitrile without using solvent and it is designated as Sol-0, where Sol = solvent. The material to liquor ratio 1 : 10 was maintained throughout the study.

Vertical wicking test

The wicking height of untreated and treated fabrics was measured according to DIN 53924 method.¹⁸ A strip of fabric (200 mm × 25 mm) was suspended vertically with its bottom side (30 mm) immersed in a reservoir of distilled water, to which 1% reactive dye (Prussian blue) was added for tracking the movement of water and after 3 min the distance of water rise in fabric was measured and reported in centimeters (cm). For each sample five tests were carried out in warp and weft direction and average was taken. Higher wicking values show greater liquid water transport ability.

XRD

XRD measurements were performed on an X'Pert PRO diffractometer system with Cu K α radiation ($\lambda = 0.15418$ nm). Crystallinity index (CrI) and crystal size of cellulose were calculated by using the following equations¹⁹:

$$\%CrI = 100[(I_{002} - I_{am})]/I_{002} \quad (1)$$

where I_{002} is the intensity of the principal Cellulose I peak at $2\theta = 22^\circ$ and I_{am} is the intensity attributed to amorphous cellulose given at $2\theta = 18^\circ$.

$$L_{hkl} = K\lambda/\beta \cos \theta \quad (2)$$

where L_{hkl} is the size of crystallites from the normal direction of hkl plane; factor k is the Scherrer constant (0.94); λ is the wavelength of the X-ray used; β represent halfwidths of the peak and 2θ is the Bragg angle.

Thermal analysis

DTA and TG were carried out using computer-controlled Perkin-Elmer Diamond instrument with a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere. All the experiments were carried out with the same nitrogen flux.

AFM

A commercial multimode sample-scanning AFM model (di CP-II Veeco, USA) was used for imaging the surface of the cotton specimens. All the AFM images were obtained in the contact mode with a silicon nitride cantilever at a scanning speed of 1.0 Hz and a scanning range setting of 5000×5000 nm² under the temperature of 25°C and RH 65%.²⁰

RESULTS AND DISCUSSION

Vertical wicking test

The wicking height (cm) of modified samples were measured and reported in the Table I. Initially, the wicking height of scoured sample showed 0.95 cm and after alkali swelling (mercerized) the height increased to 2.63 cm, which may be due to the more swelling nature of alkali treated one. After cyanoethylation (Sol-0), the sample showed lower wicking height (1.35 cm) than the mercerized sample. This can be explained as the high degree of hydrophobic nature of nitrile group may block the water molecules movement. With the addition of 2 mL of acetone (AE-2), the wicking height was increased to 1.93 cm and for EL-2 it was increased to 1.45 cm, which may be due to the formation of hydrophilic nature of amide group¹⁶ that enhance the swelling with water. A highest of 3.35 and 5.38 cm was obtained with 8 mL of acetone- and ethanol-treated fabrics, respectively. The wicking height of 2.18 cm was obtained for AE-10 and 2.30 cm for EL-10, both was higher than scoured sample (Table I). It clearly shows that the treatment with solvent can increase the wicking height after swelling with mercerizing strength of alkali.

XRD analysis

The crystallinity index and crystallite size values were reported in Table I. The scoured fabric with diffraction peaks at 14.8° , 16.4° , 22.6° , and 34.5°

TABLE I
Wicking Height, Crystallinity Index, and Crystallite Size of Modified Fabrics

Sample	Wicking height (cm)		Crystallinity index (%)		Crystallite size (nm)	
	Acetone	Ethanol	Acetone	Ethanol	Acetone	Ethanol
Scoured	0.95	–	85.4	–	7.3	–
Mercerized	2.63	–	80.0	–	6.9	–
Sol-0	1.35	–	61.6	–	8.9	–
Sol-2	1.93	1.45	67.9	62.5	5.0	6.6
Sol-4	2.28	2.78	62.8	65.5	4.9	3.4
Sol-6	2.90	4.23	63.2	65.1	4.9	6.9
Sol-8	3.35	5.38	64.1	75.3	3.3	6.7
Sol-10	2.18	2.30	70.9	78.6	6.8	3.9

Sol = Solvent.

shows the characteristic crystalline form of Cellulose I with crystalline index (CrI) of (85.4%), which is in good agreement with previous reports.²¹ After mercerization, the diffractions at 2θ of 11.9° , 20.2° , and 21.8° were observed, which can be assigned to the typical diffractions of Cellulose II with CrI of 80% that shows the crystalline transformation of cotton cellulose occurred during the mercerization, i.e., from Cellulose I–II. Moreover, in comparison with the scoured fabric, the peak intensity of the mercerized fabric obviously decreased, showing a decrease in crystallinity. This may be due to the damage of hydrogen bond system in the network structure of cotton fiber during mercerization.²²

For cyanoethylated (Sol-0) sample, in which cyanoethyl group was substituted, the peak at 19.6° and 22.1° has equal height and half widths of the peak also increased than the mercerized sample. The substitution of cyanoethyl group has reduced the density of hydrogen bonds and partially destroyed the structure of cellulose. The CrI has declined markedly (61.6%) because of the $-\text{OH}$ group in the texture of cellulose getting substituted with cyanoethyl group.

There was an increase in CrI 67.9 and 62.5% for AE-2- and EL-2-treated samples, respectively. This value is greater than cyanoethylated sample. The increased crystallinity in cotton with increase in solvent concentration may be due to the formation of amide group,¹⁶ which will facilitate the hydrogen bond formation. These are accordance with previous report,²³ which states that there was an increase in crystallinity due to the crosslinking with dimethyl dihydroxy ethylene urea (DMDHEU) and citric acid (CA).

With further increase of solvent (AE-4, AE-6, and AE-8), the CrI values were decreased. This may be due to the formation of more amide groups by solvent hydrolysis.²¹ Results of decreased crystallinity with hydrolysis are similar with those of Yin et al.²¹ who reports that the degree of crystallinity of modified cellulose declined markedly when the abundant

$-\text{OH}$ group in the texture of cellulose was substituted by urea. Moreover the diffraction peaks at 14.8° and 16.4° , which are the characteristic peaks for Cellulose I have almost disappeared. The CrI of 70.9% was obtained with 10 mL acetone treated sample (AE-10); this value was 15% higher than the Sol-0 sample. This shows that in presence of alkali, treatment with acetone will considerably reduce the crystallinity of cellulose. This was also evidenced from the wicking height (Table I).

For EL-4- and EL-6-treated samples, there was no change in CrI values. With further addition of ethanol (EL-8) the CrI value increases. The EL-10 sample shows same XRD curves as that of mercerized sample. Moreover the diffraction peaks at 12.1° , 20.2° , and 22.6° which are characteristic peaks for Cellulose II have almost reappeared for this sample and the CrI value shows only slightly lower (1.4%) than the mercerized sample. This shows that in presence of alkali, treatment with ethanol have little effect on the crystallinity of cellulose. This was also evidenced from the wicking height, in which the mercerized and EL-10 sample has small variation (Table I).

The crystallite size of modified cellulose is given in Table I. The well-defined sharp peaks in all the spectra indicate that modified cellulose is crystalline. The cyanoethylated sample has the crystallite size of 8.9 nm. The size of acetone and ethanol treated samples is ranging from 3 to 7 nm.

Thermal analysis

The initial and final decomposition temperature, weight loss and charring temperature of modified fabrics are summarized in Table II. It is known that cellulose can be heated for many hours up to 120°C without any adverse effects. It has been noted that thermal stability of cellulose and modified cellulose depends mainly on its crystallinity.²⁴ However in dry air at higher temperatures, considerable depolymerization takes place accompanied with the

TABLE II
Thermal Parameters of Modified Fabrics

Sample	Initial temp range (°C)		Weight loss (%)		Final temp (°C)		Weight loss (%)		Charring temp (°C)	
	Acetone	Ethanol	Acetone	Ethanol	Acetone	Ethanol	Acetone	Ethanol	Acetone	Ethanol
Scoured	267–395	–	71	–	543	–	20	–	573	–
Mercerized	284–394	–	70	–	569	–	19	–	596	–
Sol-0	236–384	–	78	–	542	–	14	–	575	–
Sol-2	225–379	256–374	70	66	543	538	12	18	572	585
Sol-4	243–396	222–437	70	62	597	540	18	27	627	581
Sol-6	248–394	252–386	68	65	633	503	20	24	664	549
Sol-8	259–394	273–391	70	68	578	526	17	19	612	561
Sol-10	277–384	272–390	65	66	517	529	26	24	562	564

formation of carbonyl and carboxyl groups in the solid material with the evolution of water, carbon monoxide, and carbon dioxide, and a loss of tensile strength.^{25–27} The pyrolysis of cellulose is a very complex chemical process and is commonly believed to involve two different mechanisms.²⁸ One of the processes is the dewatering and charring of cellulose, which produces H₂O, CO₂, and solid residues. The second mechanism produces the nonvolatile liquid L-glucose by depolymerization and the L-glucose cleavage is thought to continue, producing low molecular weight products, which are more flammable. The competition of these two reactions exists throughout the thermal decomposition of cellulose.²⁹

It was observed that initially scoured cotton loses 5% of weight up to 120°C due to evolution of the moisture and thereafter, it was stable up to 265°C with further 5% weight loss. Then the fabric degrades rapidly with further rise in the temperature. The decomposition of cellulose begins at 267°C and ends at 395°C with 71% weight loss (Table II). The final decomposition ends at 541°C similar to the previous reports.³⁰

The mercerization method increases the final decomposition temperature (563°C) thereby increases the thermal stability than the scoured sample. This can be explained by increase of hydrogen bonding which increases the formation of crystallinity of

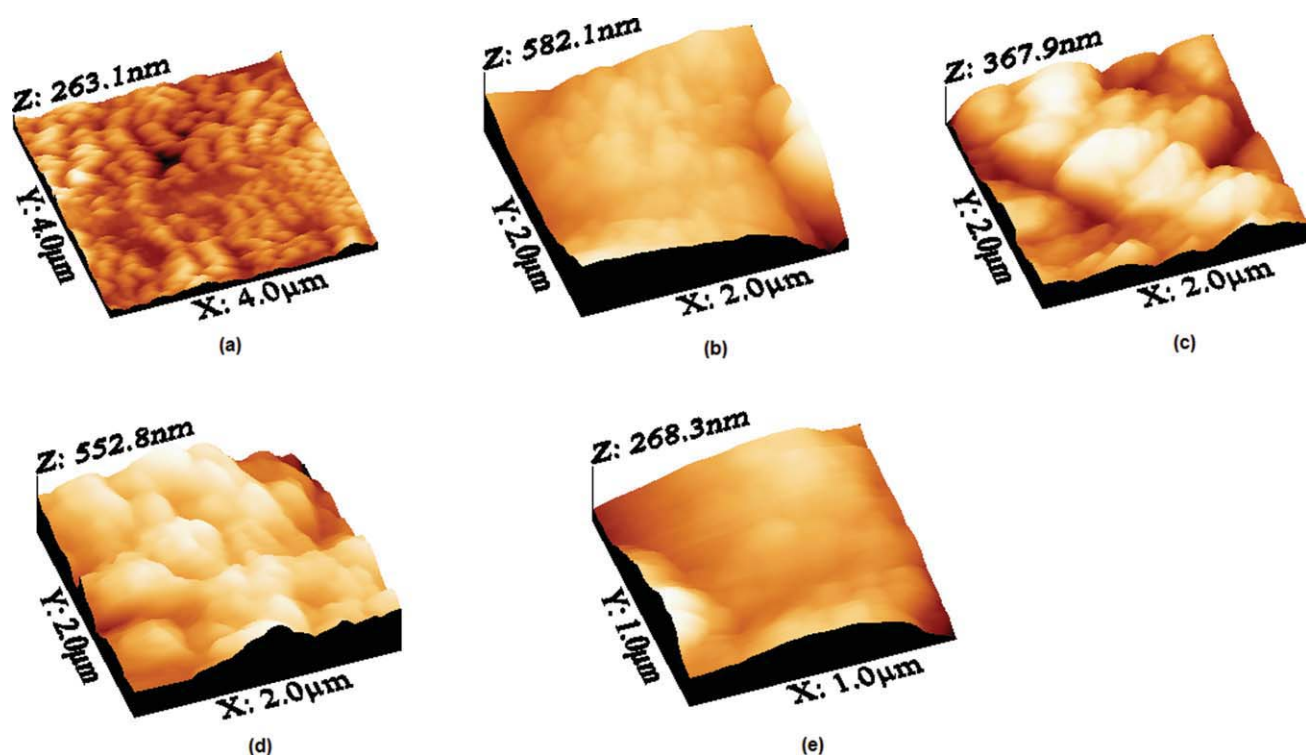


Figure 1 AFM images of (a) Scoured, (b) Mercerized, (c) Sol-0, (d) AE-2, and (e) EL-2 samples. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE III
Surface Roughness Analysis of Modified Fabrics

Sample	RMS surface roughness (nm)		Average height (nm)		Average roughness (nm)	
	Acetone	Ethanol	Acetone	Ethanol	Acetone	Ethanol
Scoured	62.03	–	180.96	–	49.08	–
Mercerized	64.11	–	363.02	–	48.36	–
Sol-0	71.58	–	217.08	–	59.47	–
Sol-2	83.11	34.29	362.92	153.36	65.09	25.75

cellulose, and consequently this increase the thermal stability.³¹ Whereas, the cyanoethylated (Sol-0) sample shows the decomposition temperature of 267°C to dehydration and depolymerization of cellulose with 14% weight loss and final decomposition temperature at 542°C to decomposition of volatile products with 95% weight loss. It has been reported that thermal stability of cellulose and modified cellulose depends mainly on its crystallinity.^{26,32} In the present study, on substitutions of hydrophobic nature of nitrile group, the crystalline lattice of the fiber was disturbed and thereby reduction in thermal stability. The same observation was made for acetone- and ethanol-treated samples and the initial decomposition temperature increases with addition of solvent. This can again be explained because of disturbance in the crystal lattice of cyanoethyl cellulose fiber on hydrolysis. A maximum charring temperature of 585°C in the EL-2 fabric and 664°C in AE-6 was noted (Table II).

AFM studies

SEM can be used to observe the surface characteristics of modified cotton fabrics, but it cannot provide information on height and roughness of the sample surface. Atomic force microscopy (AFM) can gener-

ate fine surface topographies of samples at atomic resolutions and, moreover there have been no reports on the characterization of the surface of modified cotton using this technique. The AFM images were obtained in the contact mode with a silicon nitride cantilever at a scanning speed of 1.0 Hz and a scanning range setting of 5000 × 5000 nm² under ambient conditions are shown in the Figure 1. The images of scoured, AE-0 and AE-2 and EL-2 cotton fabric were obtained between 300 and 400 nm in the 3D view (Fig. 1). All of them are of different morphology when compared with that of scoured sample. This clearly demonstrates that the solvent treatment affects the particles size. Roughness analysis of AFM images (Table III) showed that the mercerized sample has the greatest surface roughness followed by EL-2, AE-2, scoured and cyanoethylated sample. The surface roughness profile was drawn by using the reported software³³ and is shown in the Figure 2.

CONCLUSIONS

Scoured cotton fabrics were modified using acrylonitrile/acetone and acrylonitrile/ethanol mixture. The wicking height increases with increase of solvent content and a highest of 5.38 cm was obtained with 8 mL ethanol content. The crystallinity index and crystallite size show a remarkable reduction with solvent treatment and maximum change was noticed with acetone treatment. With addition of solvent, the initial and final degradation temperatures were increased considerably compared with the scoured sample. The maximum final degradation temperature (633°C) and charring temperature (664°C) were noticed for 6 mL acetone-treated sample. AFM study reveals that RMS surface roughness and average roughness values of ethanol-treated samples were less than half of the acetone-treated samples.

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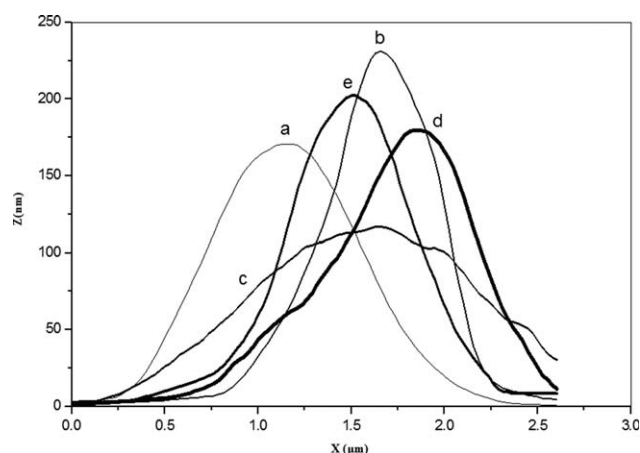


Figure 2 Roughness profile of (a) Scoured, (b) Mercerized, (c) Sol-0, (d) AE-2, and (e) EL-2 samples.

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