

Solvent-Induced Partial Cyanoethylation and Hydroxylation of Cyanoethyl Group

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ABSTRACT: An investigation has been made on the cyanoethylation of cotton fabric using aqueous sodium hydroxide with acrylonitrile in presence of solvents acetone and ethanol at different concentrations. The hydrolysis of β -cyanoethyl ether of cyanoethylated fabric in presence of solvents is studied. The rate of hydrolysis is enhanced by acetone and ethanol concentration. The formation of various products during hydrolysis is analyzed by infrared spectroscopy

copy method while scanning electron microscopy follows the variations in surface morphology. Some of the physical and chemical properties are also studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 183–191, 2006

Key words: cyanoethylation; solvents; hydrolysis; infrared spectroscopy

INTRODUCTION

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, highly accessible or decrystallized cotton fibers can be obtained.¹ One of the substitution reaction, cyanoethylation, is the permanent attachment of chemical groups to the basic unit of fiber structure to form β -cyanoethyl cellulose. Cyanoethylation of cellulose with acrylonitrile was patented in 1938^{2,3} and an extensive research work^{4–12} has been done for imparting new properties like resistance to heat, organic acids, and microorganisms. In earlier studies, Daul et al.¹³ studied the effect of diluents such as water, tertiary butyl alcohol, and benzene on the reaction rate of partial cyanoethylation of cellulose. More recently Saha and Mitra¹⁴ dealt with cyanoethylation of jute fiber in presence of benzene and dioxane.

Because of the high degree of hydrophobicity of nitrile group and lack of segmental mobility resulting from intensive molecular orientation, cyanoethylated cotton fabric has certain disadvantages such as relatively low crease recovery, poor dyeability, and low moisture absorption. Studies have been made to overcome these by incorporating comonomers, blending with other polymers, and hydrolyzing the $C\equiv N$ group.^{15,16} In the present investigation, an attempt has been made to modify the cyanoethylated cellulose structure by hydrolyzing the cyanoethyl group to get

effective dyeing at neutral pH condition with reactive dyes¹⁷ without reduction in properties obtained by means of cyanoethylation process. For this purpose, a new method of cyanoethylation process is followed by the addition of acrylonitrile and solvent with various proportions to study the influence of solvents on hydrolysis and the extent of fiber modification. The characterization of the modified cotton fiber was carried out to understand the reaction mechanism.

MATERIALS AND METHODS

Scoured plain weave cotton fabric (Area: 30×24 cm²; Ends/in. : 140; Picks/in. : 80, Count: 40 s, Weight/sq cm – 0.015 g) was used through out the study. All the chemicals used were laboratory grade. Surgical spirit was used for ethanol treatment.

Partial cyanoethylation

The scoured cotton fabric was kept immersed in aqueous sodium hydroxide (18% W/V) solution for about 30 min at room temperature, squeezed well, and then treated with acetone/acrylonitrile mixture for about 30 min at room temperature. Then the fabric was squeezed well, washed, neutralized with acetic acid, washed again in water, and air-dried. The reaction mixture ratio starts with 0/10 mL and further ratios are taken with increasing/decreasing 1 mL each of the components. The material to liquor ratio 1 : 10 was maintained throughout the study.

The same method was repeated by taking ethanol/acrylonitrile mixture instead of acetone. The samples were designated as AE X and EL X, respectively,

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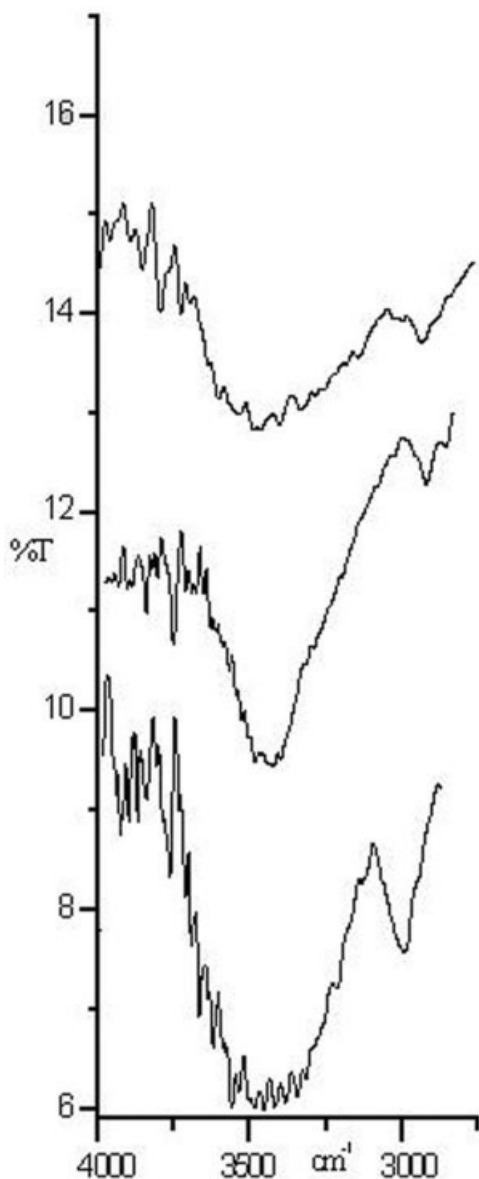


Figure 1 FTIR spectrum of modified cotton fabrics ($4000\text{--}2750\text{ cm}^{-1}$). (a) Mercerized, (b) Cyanoethylated, (c) AE2, (d) AE4.

where AE = Acetone, EL = Ethanol, and $X = 0\text{--}10\text{ mL}$ of solvent in the mixture. In the present study 0 mL of solvent treatment is cyanoethylated sample, which is common to both the solvent treated samples. This sample is taken as control sample.

Characterization and testing

Shrinkage

The fabric was marked with three pairs of datum lines in each direction and the sample was subjected to cyanoethylation.¹⁸ The initial and final dimension of the fabric in warp and weft direction was measured.

From the mean value the shrinkage percentage was calculated as follows:

Shrinkage % =

$$\frac{(\text{Scoured fabric dimension} - \text{Treated fabric dimension})}{\text{Scoured fabric dimension}} \times 100$$

Weight gain

The apparent weight gain was determined using the formula

%Weight Gain =

$$\frac{(\text{Weight of cyanoethylated fabric} - \text{Weight of scoured fabric})}{\text{Weight of scoured fabric}} \times 100$$

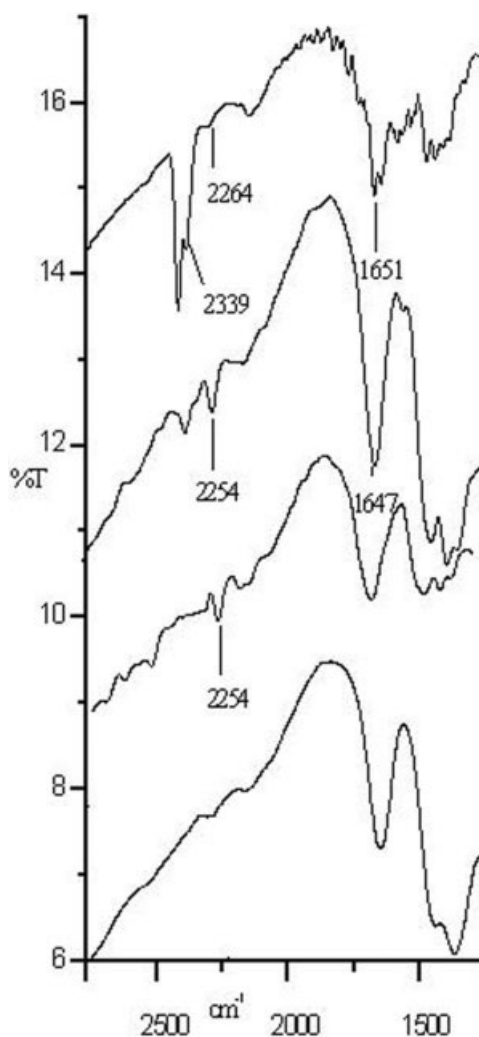


Figure 2 FTIR spectrum of modified cotton fabrics. ($4000\text{--}2750\text{ cm}^{-1}$). (a) AE6, (b) AE8, (c) AE10.

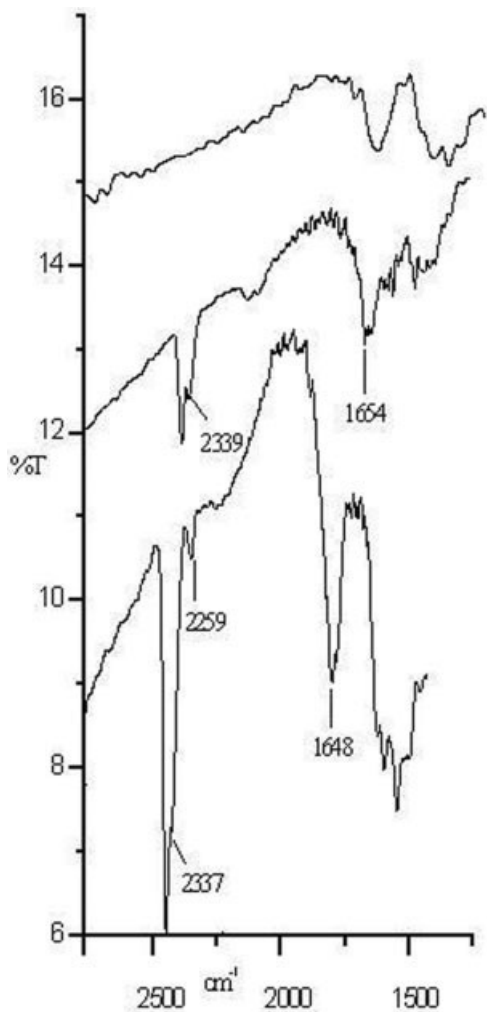


Figure 3 FTIR spectrum of modified cotton fabrics (2750–1250 cm^{-1}). (a) Mercerized, (b) Cyanoethylated, (c) AE2, (d) AE4.

Nitrogen content

Kjeldhal method^{19,20} was used to estimate the nitrogen content of cyanoethylated fabric samples. Sulfuric acid was used for digestion of the fabric.

Infrared spectroscopy

Infrared Spectra of the cut powder of the treated samples embedded in KBr were recorded with a Perkin-Elmer Spectrum RX 1 Model by the use of potassium bromide pellet technique.²¹ Intensity of the bands was measured using the base-line technique. The infrared index was calculated from the ratio of α_{1372} and α_{2900} cm^{-1} band intensity.²²

Scanning electron microscopy

The treated fabrics were examined in the scanning electron microscope (type Joel JSM 8404) after gold

coating by sputtering method. The instruments operated at 20 KV with amplification of 500 \times and 10 μm resolution.

Crease recovery

Crease recovery angle of the modified fabrics was measured by shirley crease analyzer²³ following the AATCC standard test method 66 for wrinkle recovery of fabrics. Specimens of dimension 0.6 in. wide and 1.4 in. long in warp and weft direction were prepared. They were creased on one side from which the angle was measured.

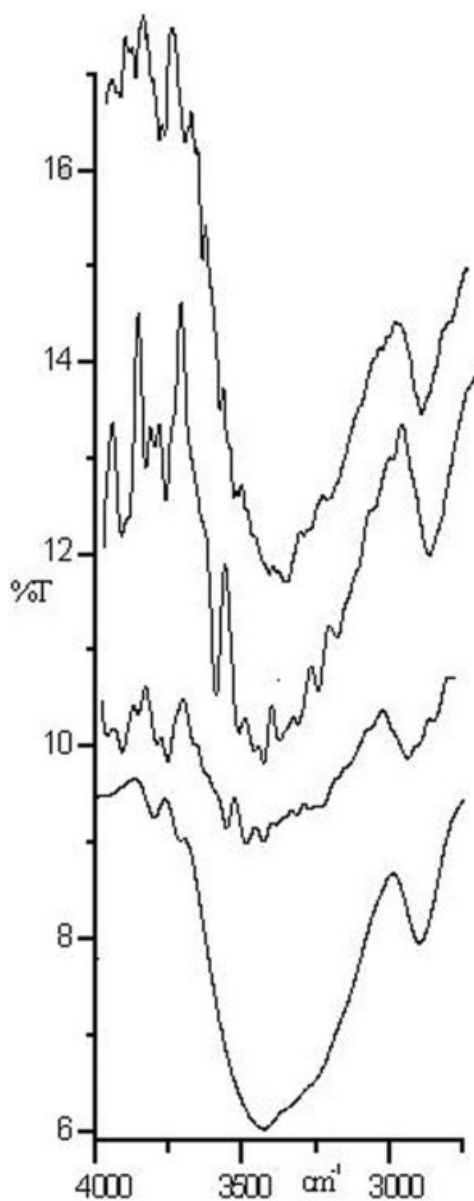


Figure 4 FTIR spectrum of modified cotton fabrics (2750–1250 cm^{-1}). (a) AE6, (b) AE8, (c) AE10.

TABLE I
FTIR Spectral Data of Mercerized and Modified Cotton Fabric (cm^{-1})

Possible assignment	AN		Acetone				Ethanol				
	10 (mL)	2 (mL)	4 (mL)	6 (mL)	8 (mL)	10 (mL)	2 (mL)	4 (mL)	6 (mL)	8 (mL)	10 (mL)
N—H Stretch	—	3415	3459	3424	3425	—	3448	3429	3454	3435	—
C—N Stretch	2254	2254	2264	2259	—	—	2255	2254	2257	—	—
C=O Stretch	—	1647	1651	1648	1654	—	—	1663	1654	1656	—
N—H (Def)	—	1500	1504	1500	1509	—	—	—	1513	1500	—
C—N Stretch	—	1429	1425	1430	1426	—	1424	1420	1431	1424	—

RESULTS AND DISCUSSION

FTIR studies

The FTIR spectra of the modified cotton fabrics have been studied to evaluate the structural changes. The IR spectra of mercerized and cyanoethylated fabrics with acetone are shown in Figures 1–4 and its characteristic peak values are given in Table I. The normal main absorbance bands of mercerized cotton fabric are at $3300\text{--}3350\text{ cm}^{-1}$, 2899 cm^{-1} , $1620\text{--}1640\text{ cm}^{-1}$, 1433 cm^{-1} , 1367 cm^{-1} , $990\text{--}1160\text{ cm}^{-1}$, and $605\text{--}695\text{ cm}^{-1}$ which correspond to hydrogen bonding and —OH-stretching, —CH-stretching, absorbed water vibration, —C—C-symmetric stretching, —CH-bending, anti-symmetric bridge —C—O—C-stretching, and —OH-out of plane bending, respectively. Fabric cyanoethylated in absence of acetone and ethanol show a band at 2254 cm^{-1} , which is attributed to the stretching vibration of $\text{C}\equiv\text{N}$ of the β -cyanoethyl group resulting from cyanoethylation as shown in the scheme 1.

With the addition of 2 mL acetone, the intensity of $\text{C}\equiv\text{N}$ peak decreases at 2254 cm^{-1} . Occurrence of multiple bands is observed at 3330 cm^{-1} region which is attributed to NH stretch. (scheme 2).

In 4 mL acetone treated fabric, the intensity of $\text{C}\equiv\text{N}$ peak reduces at 2264 cm^{-1} . Meanwhile the carbonyl band of CONH_2 appears at 1651 cm^{-1} (scheme 3).

The peak at 2339 cm^{-1} indicates the presence of amidate anion. The amidate anion formed, which is further protonated to give amide. A band appears in the region of $3200\text{--}3600\text{ cm}^{-1}$ with a maximum at 3459 cm^{-1} , which is due to the band for N—H of amide group.

In 6 mL acetone treated fabric, the appearance of band at $1500\text{--}1530\text{ cm}^{-1}$ is attributed to the N—H

stretching, which is shown in Table I. As hydrolysis proceeds, the $\text{C}\equiv\text{N}$ band disappears slowly with concurrent appearance of amide group at 1654 cm^{-1} in 8 mL acetone. Additional bands appear in the region of 1700 cm^{-1} , which may be due to the presence of amide group. These observations suggest that hydrolysis occurs in two steps. The $\text{C}\equiv\text{N}$ of the cyanoethylated fabric first converted into amidate anion, which is then converted into CONH_2 . Similar peaks are observed in 10 mL acetone, as that of mercerized cotton fabric.

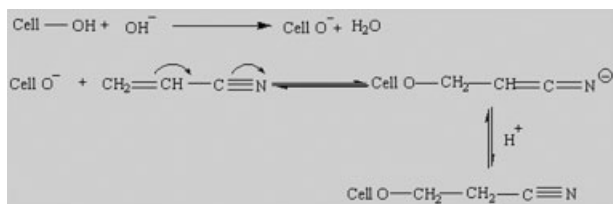
Influence of ethanol

The IR spectra of modified fabrics in presence of ethanol are shown in Figures 5–8. In the case of 2 mL ethanol, additional bands appear in the region of 3348 cm^{-1} which may be attributed to the presence of N—H stretch. In 4 mL ethanol the intensity of the peak at 2254 cm^{-1} decreases. Appearance of peak at 1654 cm^{-1} show the presence of carbonyl group amide and multiple peaks are observed in the region of 3454 cm^{-1} , which is due to the N—H stretch of amide in 6 mL ethanol.

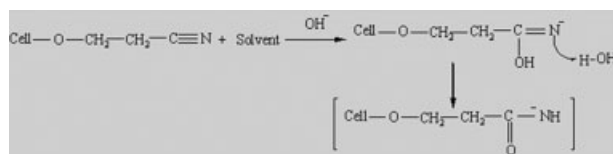
As the ethanol concentration increases, the hydrolysis becomes prominent, which leads to the appearance of band at 1656 cm^{-1} . No peak is observed at 2254 cm^{-1} in 8 mL ethanol, which suggests that $\text{C}\equiv\text{N}$ group is hydrolyzed to amide group. When the concentration of ethanol is kept at 10 mL many peaks appear almost similar to that of mercerized cotton fabric.

Scanning electron microscopy

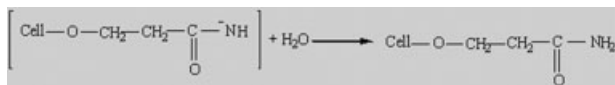
The surface morphology of the mercerized and solvent induced cyanoethylated fabrics examined by the



Scheme 1



Scheme 2



Scheme 3

scanning electron microscope is shown in Figure 9. In mercerized cotton fabric (Fig. a), as expected the fibers are having rod like shape and the surface appears to be smooth and uniform while in cyanoethylated fabric (Fig. b), the fibers are coalesced with each other. Because of the formation of cyanoethyl cellulose, the surface appears to be bulkier and nonuniform than that of mercerized fabric. The solvent assisted cyanoethylated fabric shows almost similar structure as that of mercerized fabric even after hydrolysis.

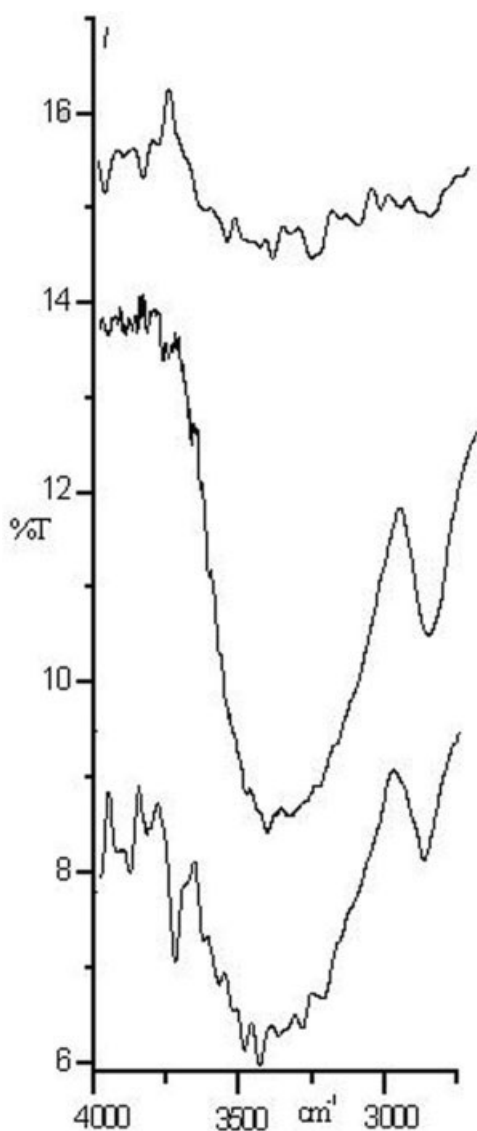


Figure 5 FTIR spectrum of modified cotton fabrics (4000–2750 cm^{-1}). (a) Mercerized, (b) Cyanoethylated, (c) EL2, (d) EL4.

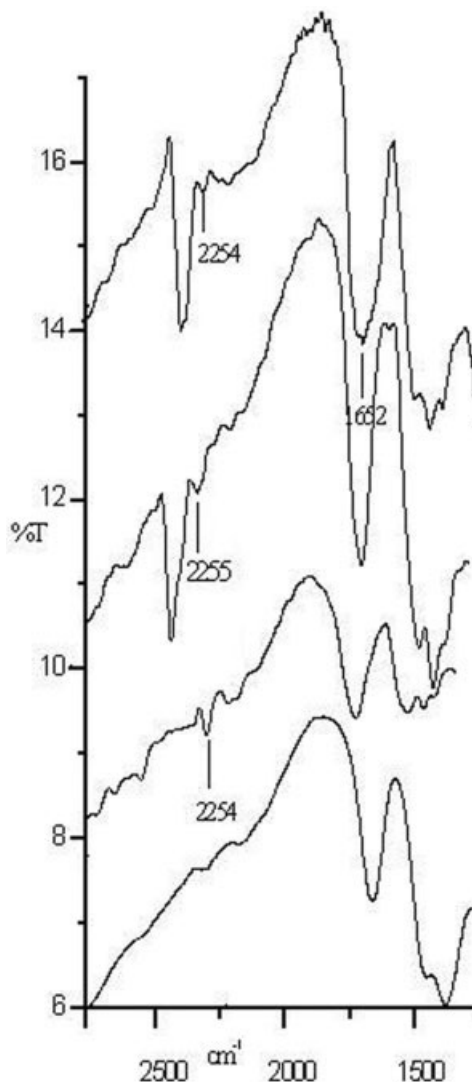


Figure 6 FTIR spectrum of modified cotton fabrics (4000–2750 cm^{-1}). (a) EL6, (b) EL8, (c) EL10.

Shrinkage

Fabric shrinkage is mainly the consequence of meta stable state of the fabric and the establishment of energy equilibrium under the influence of cyanoethylation. The reason for this meta stable²⁴ state is the induced energy state, which is maintained in the fabric by frictional, shear and tensile forces acting between fibers in yarn and between yarns in fabric. By wet treatment the fibers and yarn return to lower, more stable equilibrium state, which in turn results in the relaxation of most stresses. The consequence of this phenomenon is fabric shrinkage.

The mercerized sample shows 28% shrinkage. The shrinkage of all other cyanoethylated cotton fabric in presence of acetone and ethanol are plotted in Figure 10. It is obvious from figure that the shrinkage values of all the AEX samples are higher than that of ELX and control samples. This may be attributed to the greater

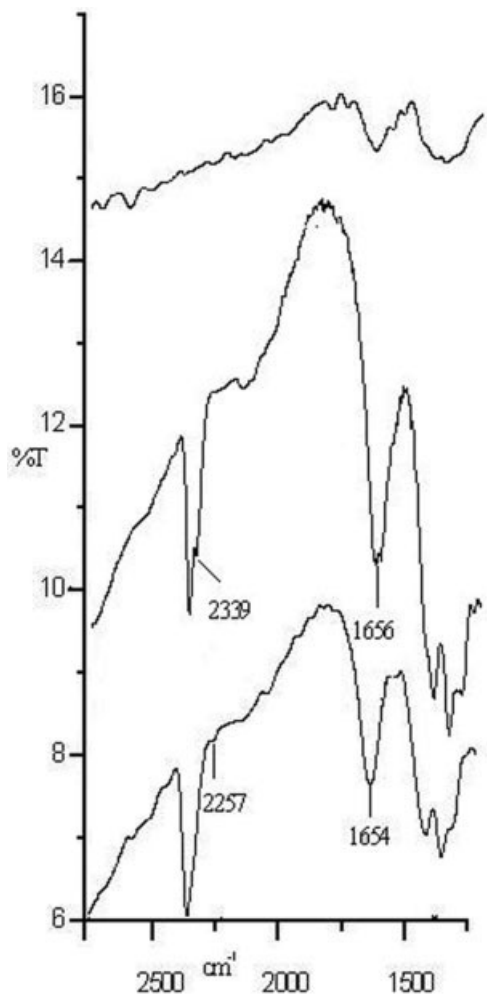


Figure 7 FTIR spectrum of modified cotton fabrics ($2750\text{--}1250\text{ cm}^{-1}$). (a) Mercerized, (b) Cyanoethylated, (c) EL2, (d) EL4.

polarity of acetone, which proves to be a stronger swelling agent than ethanol, thereby increasing the shrinkage. It is apparent that the shrinkage values of acetone-treated fabric gradually increase up to 7 mL of acetone concentration and a slight fall is observed with further increase, which may be due to the decreased extent of swelling and increased rate of hydrolysis. In the case of ethanol treatment, the shrinkage value shows an opposite trend with increase in solvent concentration. In both the cases, at 7 mL solvent concentration there is drop in shrinkage value.

Weight gain

The percentage weight gain of AEX and ELX samples are shown in Figure 11. In ethanol treatment, addition of 1 mL of solvent shows a steady increase in weight gain. With further addition of ethanol, the values show a gradual decrease and reach the control sample value at 4 mL concentration. Further addition of eth-

anol shows a considerable drop in weight gain. In the case of acetone treatment, as the concentration increases the weight gain drops compared to that of the control sample from the very beginning.

Nitrogen content

The effect of solvent concentration on the extent of the reaction is expressed as % nitrogen content, which is plotted in Figure 12. It is apparent from the graph that nitrogen content decreases with increase in solvent concentration and decrease in acrylonitrile. Cyanoethylation in presence of acetone increases the nitrogen content to a greater extent than that of ethanol. This may be due to the greater polarity of acetone. The

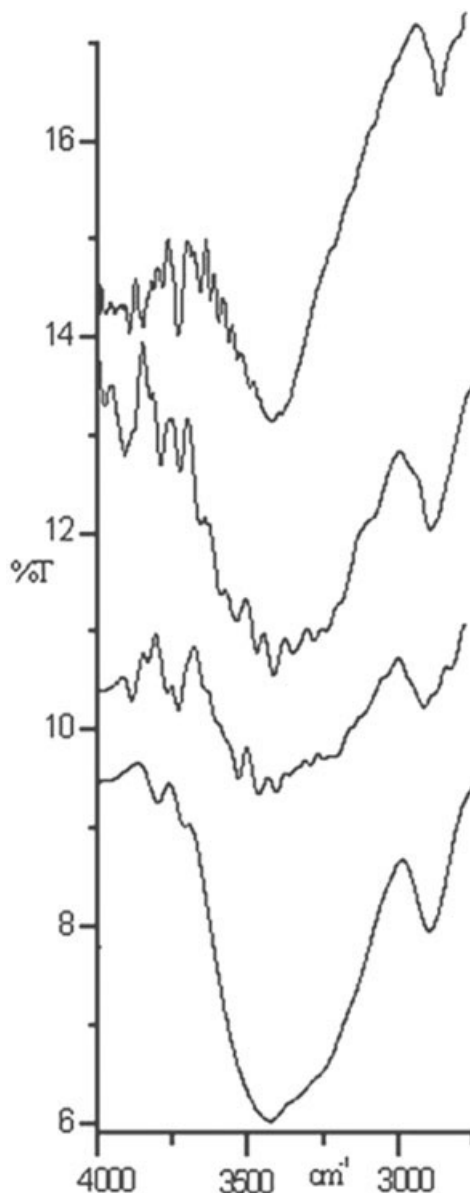


Figure 8 FTIR spectrum of modified cotton fabrics ($2750\text{--}1250\text{ cm}^{-1}$). (a) EL6, (b) EL8, (c) EL10.

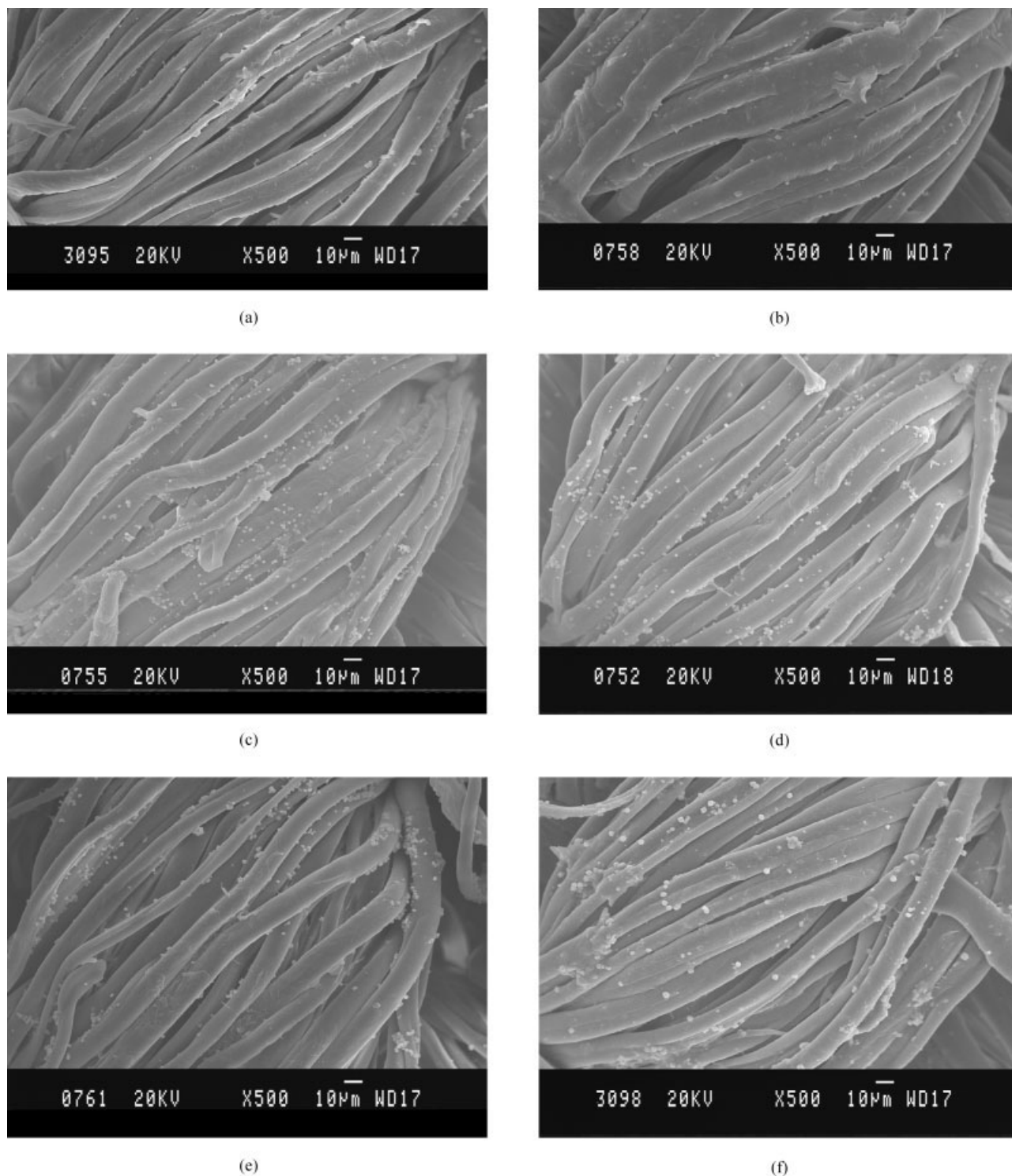


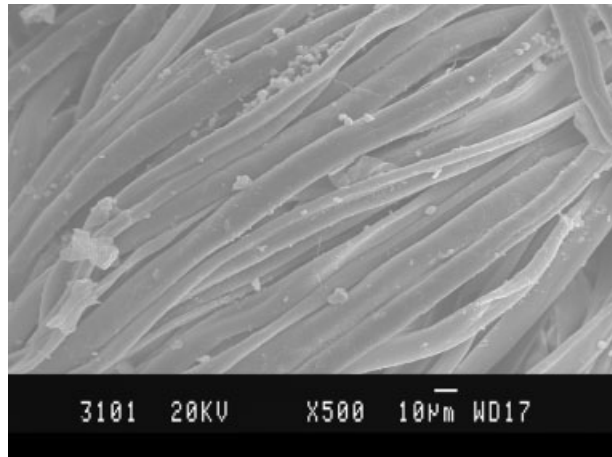
Figure 9 Scanning electron micrograph of modified cotton fabrics. (a) Mercerized, (b) Cyanoethylated, (c) AE2, (d) AE8, (e) AE10, (f) EL2, (g) EL8, (h) EL10.

addition of solvent retards the extent of the reaction by means of hydrolysis of nitrile to amide group.

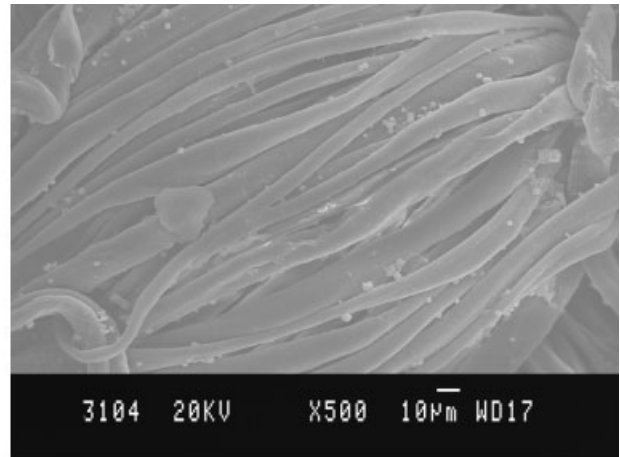
Infra red index

As a measure of crystallinity, the infrared ratio of α_{1372} and $\alpha_{2900} \text{ cm}^{-1}$ is calculated according to Nelson and

O' Connor. The infrared ratios obtained from the spectra are presented in Figure 13. It is observed that acrylonitrile treatment have reduced the crystallinity index value as observed by Hirai et al.²⁵ In acetone treatment, the infrared ratio decreases steadily up to 6 mL and then increases gradually with an increase in



(g)



(h)

Figure 9 (Continued from the previous page)

concentration. It was pointed out by Awadel-Karim et al.²⁶ that the crystallinity index increases with increase in acetone concentration during solvent treatment of cotton cellulose. The trend seems to be identical for

ethanol also. But the maximal value at 10 mL ethanol is lower than that of acetone.

Crease recovery

The crease recovery of scoured and mercerized samples is 143 and 146, respectively. The effect of varying

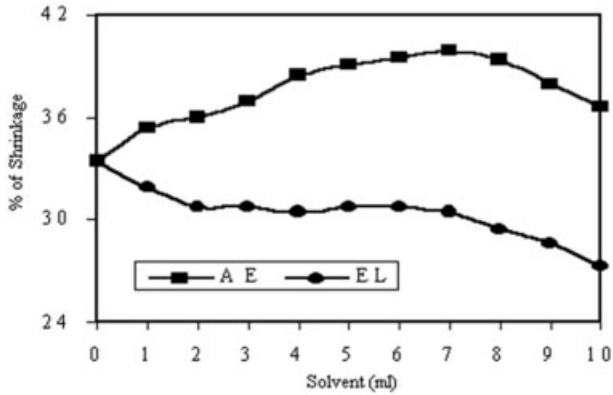


Figure 10 Shrinkage percentage of modified cotton fabrics. AE, Acetone; EL, Ethanol.

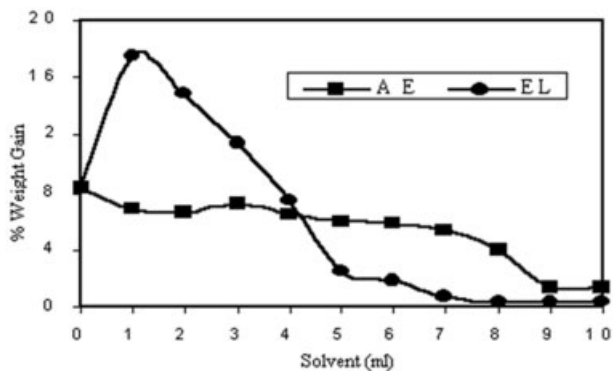


Figure 11 Weight gain of modified cotton fabrics. AE, Acetone; EL, Ethanol.

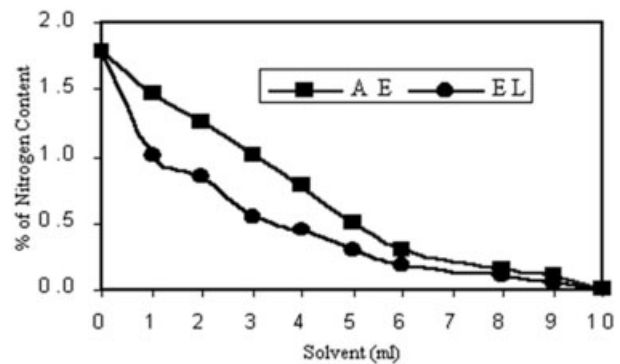


Figure 12 Nitrogen content of modified cotton fabrics. AE, Acetone; EL, Ethanol.

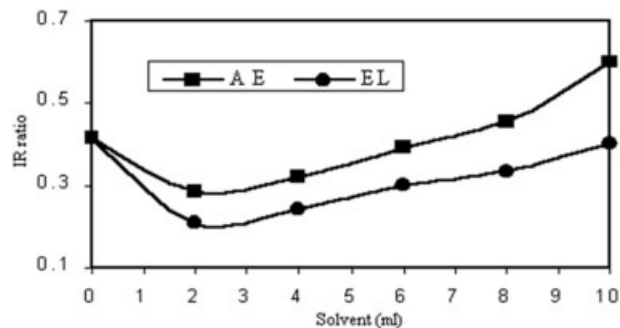


Figure 13 Infrared index of modified cotton fabrics AE, Acetone; EL, Ethanol.

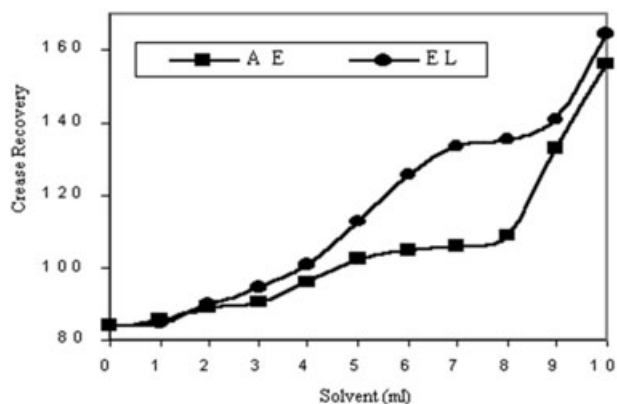


Figure 14 Crease recovery of modified cotton fabrics. AE, Acetone; EL, Ethanol.

concentration of solvent on crease recovery of cyanoethylated cotton fabrics was illustrated in the Figure 14. It is obvious that the solvent assisted cyanoethylated fabric show increased crease recovery than that of control sample. The recovery angle of the fabric treated with both the solvents seem to be similar up to 2 mL and further, there is an increment as the concentration increases. This may be due to the increase in hydrolysis of nitrile group. Cyanoethylation in presence of ethanol show a greater recovery than that of acetone. There is a correlation between the nitrogen content and crease recovery. Both the properties are inversely proportional to each other.

CONCLUSIONS

Cyanoethylation of cotton fabric with acrylonitrile in presence of acetone/ethanol enhance the hydrolysis of $C\equiv N$ group. Such treatment brings about some chemical change in the treated fabric. The infrared studies indicate the introduction of cyanoethyl group, which disappears slowly with increase in solvent concentration and *vice versa*. The spectra also depict the evidence for hydrolysis of $C\equiv N$ band to amide group, which is formed in both the solvents. The shrinkage values are higher for samples treated with acetone than that of ethanol, which may be attributed to the greater polarity of acetone. The values of nitrogen content and weight gain decrease with solvent concentration, which gives support for the extent of the reaction. With the increase in hydrolysis, the samples

indicate an improvement in the crease recovery than that of cyanoethylated samples. Scanning electron microscopy studies serve as a proof for swollen fabric. Further investigations are to be carried out to study the dyeing and other mechanical properties of the treated fabrics.

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