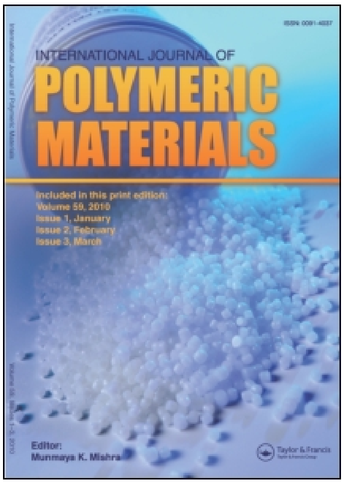

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Effect of Solvent Induced One Step Partial Cyano-Hydroxylation Process on Properties of Cotton Fabric

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The present study evaluates the effect of fabric material to solvent/acrylonitrile mixture ratio on solvent induced hydroxylation of cyanoethylated cotton fabric using solvents and acrylonitrile mixture. Some of the properties such as shrinkage, percentage of weight gain, diameter and crease recovery were studied. The surface characterization was carried out by SEM, which indicates the variations of its surface morphology after treatment.

Keywords: cotton, cyanoethylation, hydroxylation, solvents

INTRODUCTION

Cotton cellulose has excellent properties such as high water absorbency and moisture regain, being comfortable to wear and easy to dye. Much research has been carried out in the field of chemical modification of cotton cellulose to produce new and unusual properties [1]. Chemical modification of cotton cellulose, such as cyanoethylation [2–10], acetylation [11–12], carbamoylethylation [12] and grafting [13] etc, is generally performed by reaction with the functional groups already present in the fiber.

Cellulose modified chemically using acrylonitrile lack hydrophilic nature and shows certain shortcomings such as relatively low crease recovery, poor dyeability and low moisture absorption. Studies have

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been made to overcome these by incorporating co-monomers, blending with other polymers and hydrolyzing the C≡N group [14–15]. Hydrolysis of the resultant grafted cellulose has been extensively studied and the subject has been reviewed by many authors [13]. Scientists have dealt with the hydrolysis of the cyanoethyl group under various conditions with alkali and acid as the hydrolyzing agent [16–17]. Recently the formation of products during hydrolysis of β-cyanoethyl ether of the cyanoethylated fabric in presence of solvents has been studied [18].

In the present investigation, an attempt has been made to study the effect of material to mixture ratio on the properties of cotton fabrics after single step process of cyanoethylation and hydroxylation of cellulose. Cyanoethylation and hydroxylation was carried out in cotton fabric with aqueous sodium hydroxide swelling followed by solvents/acrylonitrile mixture with different material to mixture ratios such as 1:10, 1:7.5 and 1:5. The changes in their properties at each level of material to mixture ratio were analyzed.

EXPERIMENTAL

Materials and Methods

Scoured plain weave cotton fabric (Area: 30 × 24 cm; Ends/inch: 140; Picks/inch: 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.

One Step Cyano Hydroxylation Process

The scoured cotton fabric was kept immersed in aqueous sodium hydroxide (18% W/V) solution for about 30 minutes at room temperature, squeezed well and then treated with acetone/acrylonitrile mixture for about 30 minutes at room temperature. Then the fabric was squeezed well, washed, neutralized with acetic acid, washed again in water and air-dried. For convenience and comparison, the solvent/acrylonitrile mixture ratio was set with 0/10, 2/8, 4/6, 6/4, 8/2 and 10/0 ml. Based on 1:10, 1:7.5 and 1:5 material to liquor ratio, the treatment solution (acetone/acrylonitrile and ethanol/acrylonitrile) was taken by multiplying the mixture ratio with the number of 1, 0.75 and 0.5 for the respective material to mixture ratios. A specially fabricated closed rectangular stainless steel trough was used for all the treatments. The samples were designated as mlr10, mlr7.5 and mlr5 where mlr = material to liquor ratio.

Characterization and Testing

Shrinkage

The fabric was marked with three pairs of datum lines in each direction and the sample was subjected to cyanoethylation. The initial and final dimension of the fabric in warp and weft direction was measured [19]. From the mean value the shrinkage percentage was calculated as follows:

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

Weight Gain

The apparent weight gain was determined using the following formula

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

Diameter Measurements

Diameter was measured using Metz-782 model projection microscope having an attachment to guide the yarn under proper tension with a magnification of 50×. Ten yarns of 10 cm length in each warp and weft directions were taken from the fabric sample. For each yarn direction 50 readings were taken and the average was reported.

Nitrogen Content

Kjeldhal method [20–21] was used to estimate the nitrogen content of the cyanoethylated cotton fabric samples. Sulphuric acid was used for digestion of the fabric.

Crease Recovery

Crease recovery angle of the modified fabrics was measured by Shirley crease analyzer [22] following the AATCC standard test method 66 for wrinkle recovery of fabrics. Specimens of dimension 0.6 inch wide and 1.4 inch long in warp and weft direction were prepared. They were creased on one side from which the angle was measured.

Scanning Electron Microscopy

The treated mlr10 samples were examined in the scanning electron microscope (Joel JSM 8404) after gold coating by the sputtering method. The instruments were operated at 20 KV with amplification of $\times 100$ and $10\,\mu m$ resolution.

RESULTS AND DISCUSSION

Shrinkage

Fabric shrinkage is mainly a consequence of the meta-stable state of the fabric and the establishment of energy equilibrium under the influence of cyanoethylation. The reason for this meta-stable [23] state is the induced energy state, which is maintained in the fabric by frictional, shear and tensile forces acting between fibers in the yarn and between yarns in the 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.

Figure 1 shows the percentage shrinkage of modified cotton fabric with different concentration of acetone (AE). From the graph, it is noted that for mlr10, the percentage of shrinkage increases up to 8 ml and suddenly drops at 10 ml. This may be attributed to the increase in acetone concentration, which leads to increased extent of hydrolysis and swelling. The curve of mlr7.5 shows the same trend.

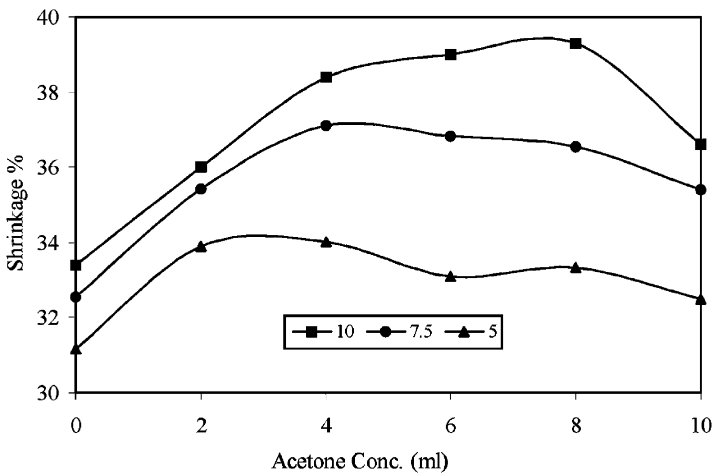

FIGURE 1 Shrinkage percentage of cotton fabric modified using acetone.

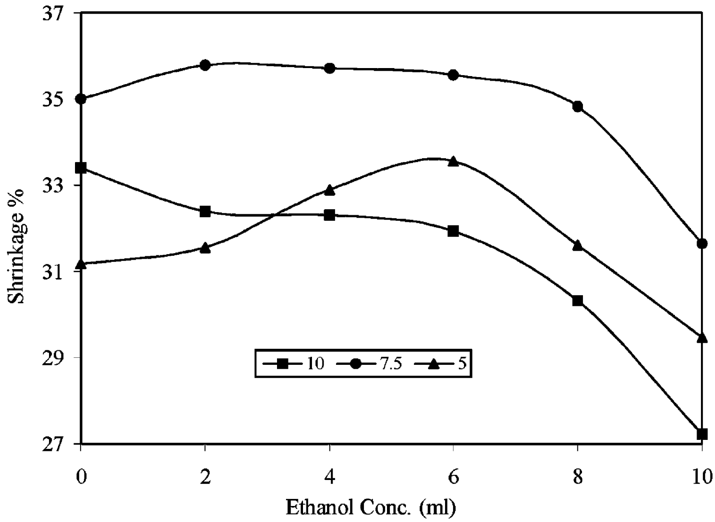

FIGURE 2 Shrinkage percentage of cotton fabric modified using ethanol.

In mlr5, the plot increases with acetone concentration and a drop is noted at 6 ml and then the shrinkage percentage decreases gradually.

The percentage of shrinkage on varying the ethanol (EL) concentration is shown in Figure 2. For mlr10 samples, the curve shows a gradual decrease as the concentration of ethanol increases. The same trend was also noticed for mlr7.5 and, more or less, for mlr5. The decrease is due to the increase in swelling of the fabric with increase in ethanol concentration.

The shrinkage values of modified cotton fabric in presence of acetone and ethanol with mlr7.5 is given in the Figure 3. It is obvious from the graph that when the solvent concentration increases the percentage of shrinkage also increases gradually up to 8 ml and then drops at 10 ml of solvent. The shrinkage values of acetone treated samples are higher than those of ethanol treated samples. This may be attributed to the greater polarity of acetone than that of ethanol. Figure 4 shows the percentage of shrinkage obtained by mlr5. Both solvents increase gradually up to 4 ml and a drop is observed in 6 ml of acetone, while in ethanol a sudden fall is noted at 8 ml.

Weight Gain

The percentage weight gain of the modified fabric with mlr10, mlr7.5 and mlr5 are shown in Figure 5. In the case of mlr10 treatment, as the

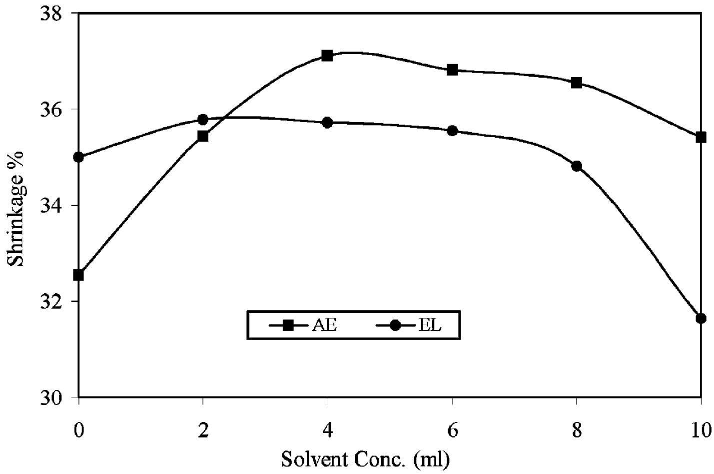

FIGURE 3 Shrinkage percentage of solvent modified cotton fabric (mlr7.5).

concentration of acetone increases the weight gain drops from the very beginning. This trend can be explained by the fact that as the acetone concentration increases the extent of hydrolysis of CN group, an increase which leads to the decrease in weight gain. The plots of mlr7.5 and mlr5 follow a similar trend.

In ethanol treatment, addition of 2 ml of the solvent shows an increase in weight gain, which is noted from Figure 6. With further

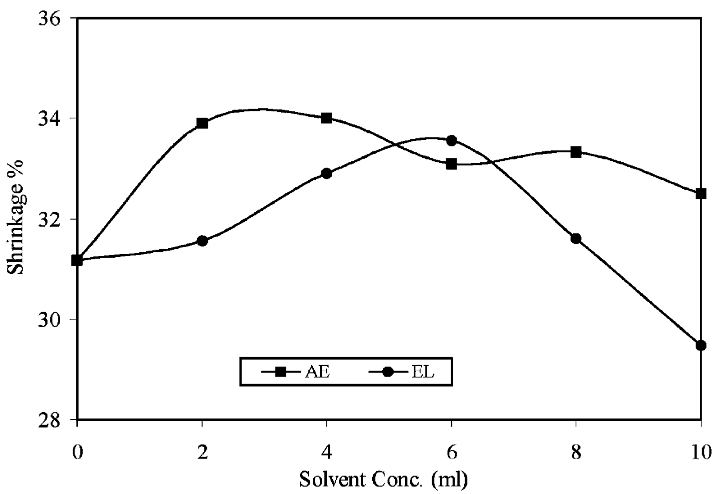

FIGURE 4 Shrinkage percentage of solvent modified cotton fabric (mlr5).

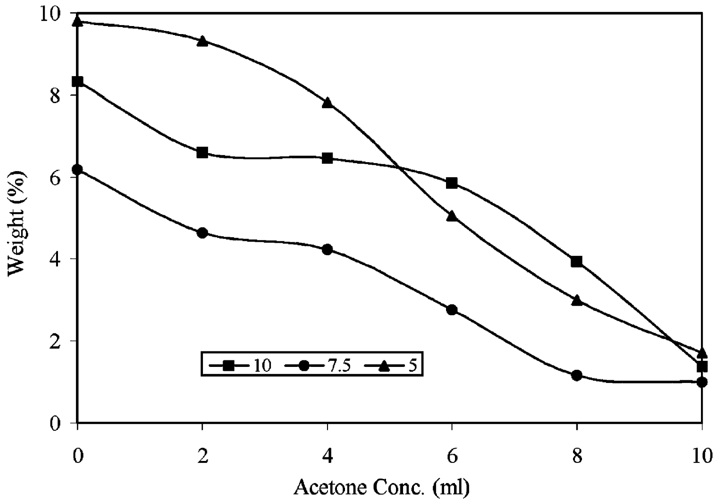

FIGURE 5 Percentage of weight gain on acetone modified cotton fabric.

addition of ethanol, a considerable drop in weight gain is noted. In mlr7.5 and mlr5 treatment, the plot shows an increase in addition of 2 ml of ethanol and then decreases.

Figure 7 indicates the percentage of weight gain on the concentration of solvent. From the plot it is noted that in mlr7.5, the percentage of weight gain decreases gradually with acetone concentration.

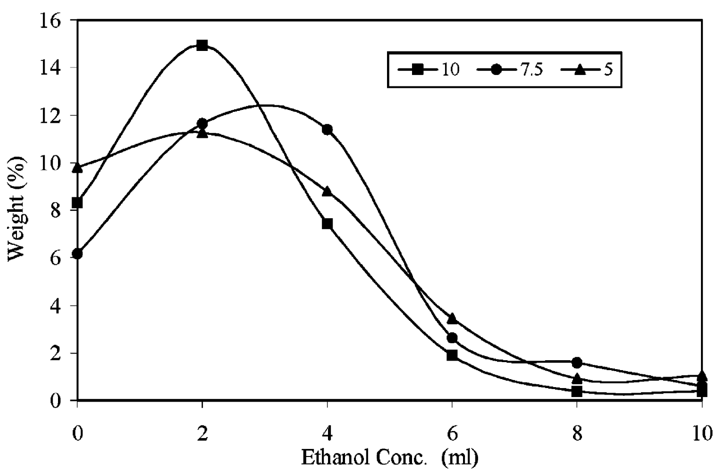

FIGURE 6 Percentage of weight gain on ethanol modified cotton fabric.

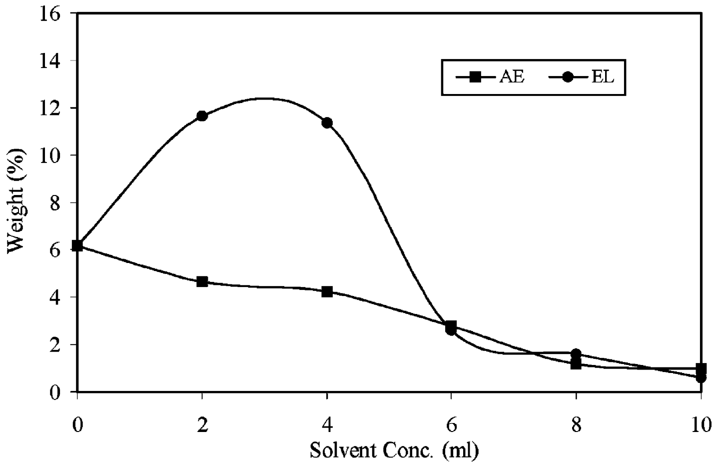

FIGURE 7 Percentage of weight gain on solvent modified cotton fabric (mlr7.5).

This can be explained by the fact that as the acetone concentration increases the rate of hydrolysis of the cyanoethyl group also increases which results in decrease in the percentage of weight gain. In the case of ethanol, the weight gain percentage increases steadily upto 4 ml and then drops.

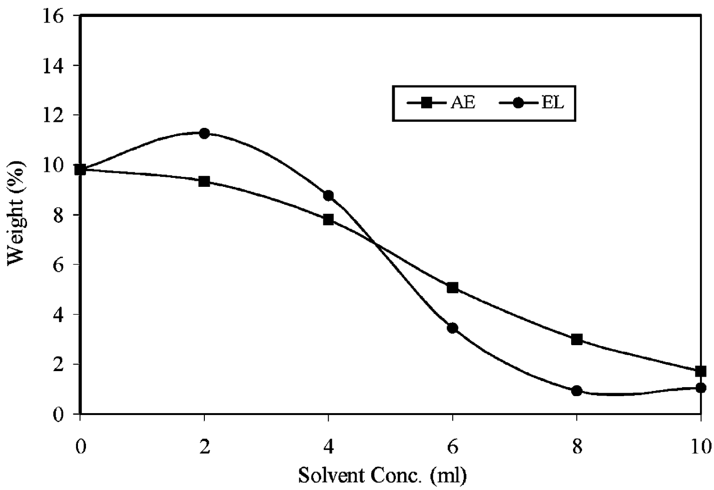

FIGURE 8 Percentage of weight gain on solvent modified cotton fabric (mlr5).

Figure 8 explains the variation of solvent concentration on the weight gain percentage with mlr5. The curve shows a steady decrease in weight gain as the solvent concentration increases.

Diameter Measurements

The diameter of yarns of the fabric in warp direction is plotted against the concentration of acetone in Figure 9. From the plot it is apparent that in mlr10, the curve shows a gradual increase with increase in concentration of acetone. This may be interpreted by the fact that as the concentration of acetone increases the swellability also increases gradually. The swelling of fiber causes an increase in diameter of the yarn. The same trend can be observed for mlr7.5 and mlr5. On comparing, the diameter is found to increase to a greater extent in mlr10 than that of the others. This may be due to the higher concentration of acetone.

The diameter of weft yarn on the acetone concentration is shown in Figure 10. It may be noted from the plot that the curve shows a steady increase as the concentration of acetone solvent increases. This indicates that swelling increases with the concentration of acetone. The yarns show the same trend for various material to liquor treatments.

Figure 11 shows the effect of the concentration of ethanol solvent on the diameter of warp yarn of the modified fabric. The yarn diameter of mlr10 increases with increased ethanol concentration. This is apparently due to the increase in swelling of the yarn as the concentration

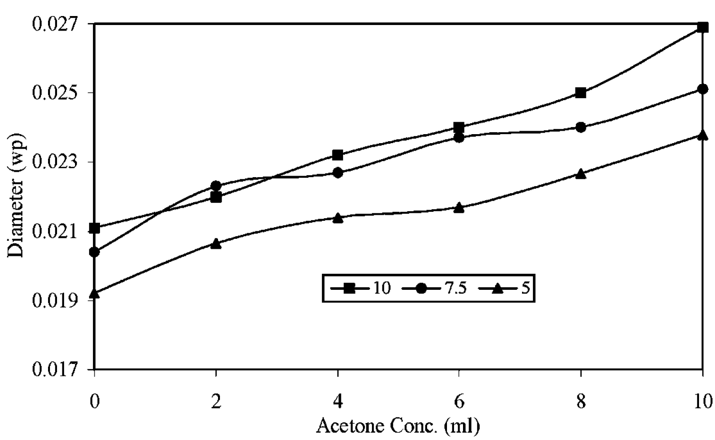

FIGURE 9 Diameter of warp yarns of cotton fabric modified using acetone.

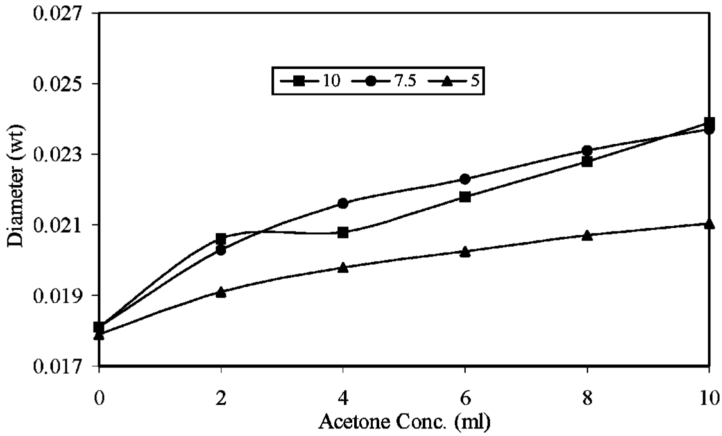

FIGURE 10 Diameter of weft yarns of cotton fabric modified using acetone.

of ethanol increases. The trend for mlr7.5 and mlr5 seems to generally be similar to that of mlr10.

The values of diameter of the weft yarn with the ethanol concentration are illustrated in Figure 12. A gradual increase is observed in mlr10 samples. This may be attributed to the fact that large quantity of solvent facilitates the increase in swellability of yarn in the fabric. The curve of mlr7.5 and mlr5 appears to generally be similar to that of mlr10.

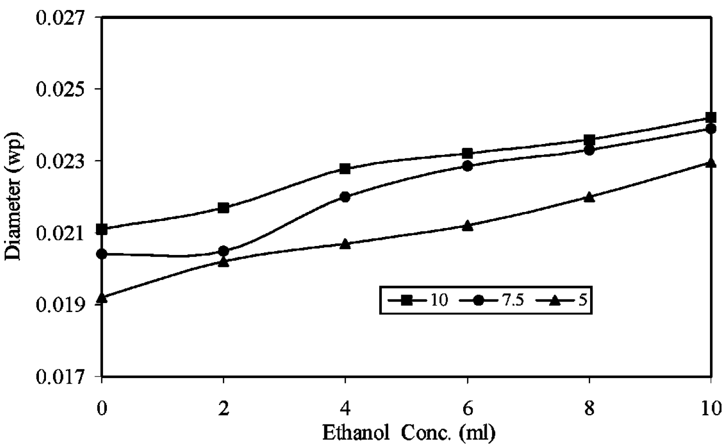

FIGURE 11 Diameter of warp yarns of cotton fabric modified using ethanol.

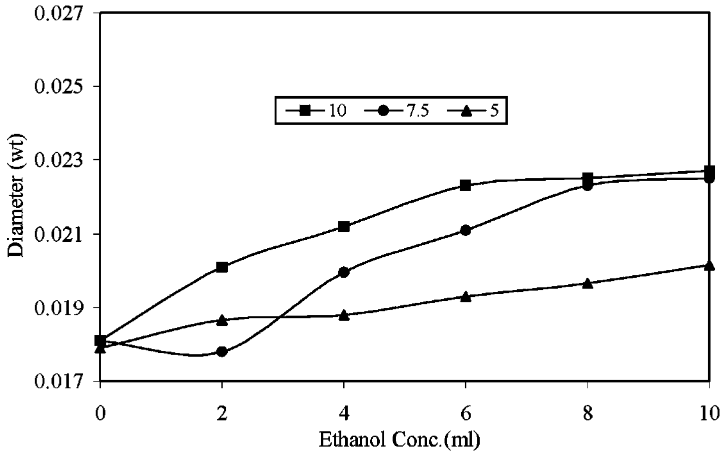

FIGURE 12 Diameter of weft yarns of cotton fabric modified using ethanol.

Nitrogen Content

The effect of solvent concentration on the extent of the reaction is expressed as percentage of nitrogen content. It is apparent from the Figure 13 that in mlr10, the nitrogen content decreases with increase in acetone concentration. This may be due to the addition of solvent, which retards the extent of the reaction by means of hydrolysis of nitrile to amide group [18]. It is noted that the plot of mlr7.5 and

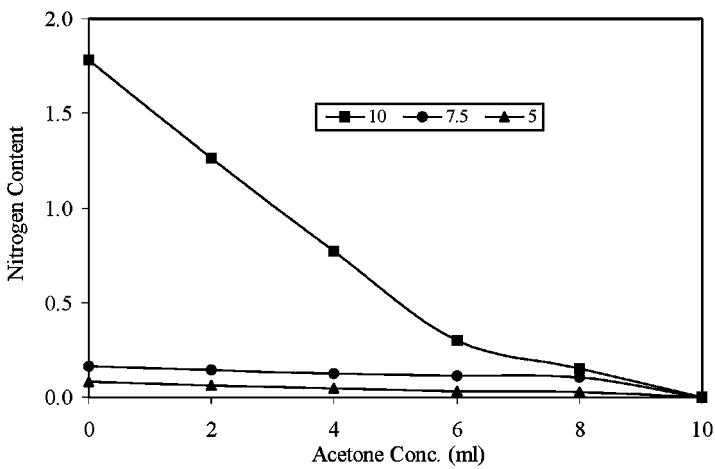

FIGURE 13 Nitrogen content of cotton fabric modified using acetone.

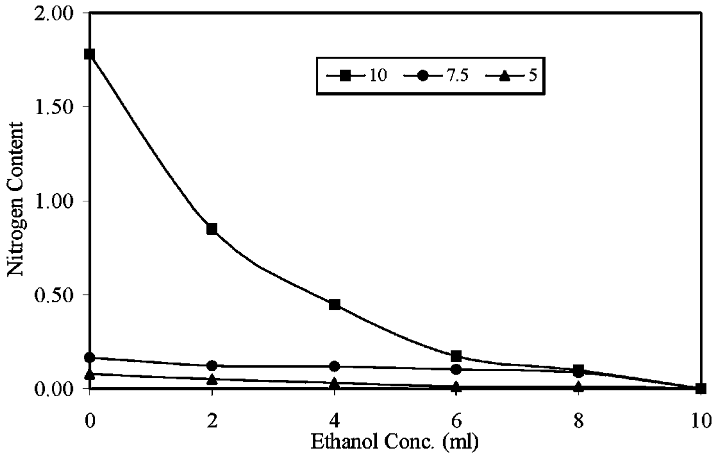

FIGURE 14 Nitrogen content of cotton fabric modified using ethanol.

mlr5 are different from that of mlr10. With increased solvent concentration the plots appear to be at constant level.

The nitrogen content of the samples against ethanol concentration is shown in Figure 14. From the graph, it is noted that in mlr10 the nitrogen content decreases with increase in solvent concentration. The plots are similar to those of acetone solvent.

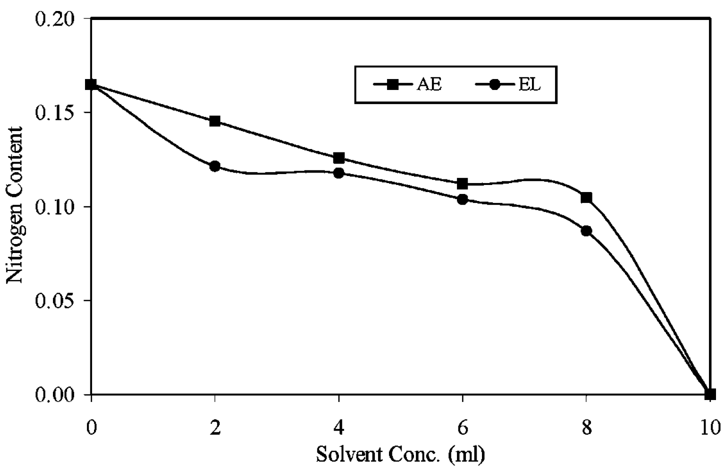

FIGURE 15 Nitrogen content of solvent modified cotton fabric (mlr7.5).

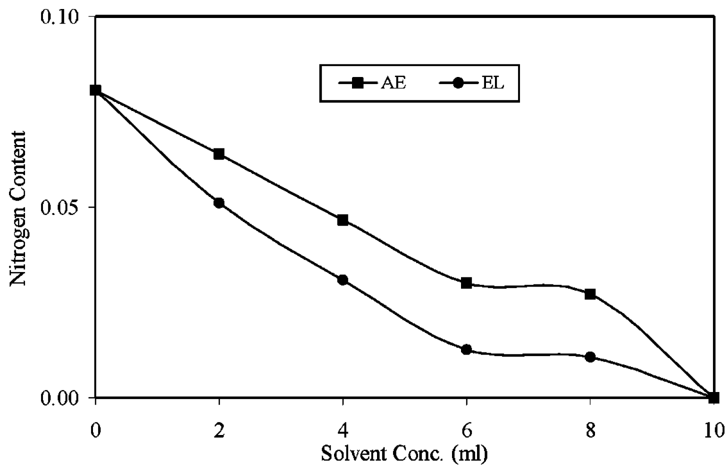

FIGURE 16 Nitrogen content of solvent modified cotton fabric (mlr5).

Figure 15 indicates that the nitrogen content decreases with the increase in concentration of the solvent. The acetone induced cyanoethylated cotton fabric shows higher nitrogen content than that of ethanol. This is due to the greater polarity of the solvent. In mlr5 the same trend can be observed in Figure 16. Due to the hydrolysis, the nitrogen content decreases with solvent concentration.

Crease Recovery

The effect of varying concentration of acetone solvent on crease recovery of cyanoethylated cotton fabric is shown in Figure 17. It is obvious from the graphs that the solvent assisted cyanoethylated fabric shows an increased crease recovery. The trend seems to be similar for all the treatments i.e., mlr10, mlr7.5, and mlr5. Crease recovery of the treated fabric increases with increase in acetone concentration. This may be because of the increase in hydrolysis of nitrile group. Cyanoethylation with mlr10 shows greater recovery than that of mlr7.5 and mlr5. There is a correlation between the nitrogen content and crease recovery. Both the properties are inversely proportional to each other.

The crease recovery of ethanol treated fabric against the concentration of the solvent is given in Figure 18. The graph is similar to that of the acetone treated fabric. The crease recovery of the solvent induced cyanoethylated cotton fabric with mlr7.5 is plotted in Figure 19. From the graph it is apparent that the recovery increases

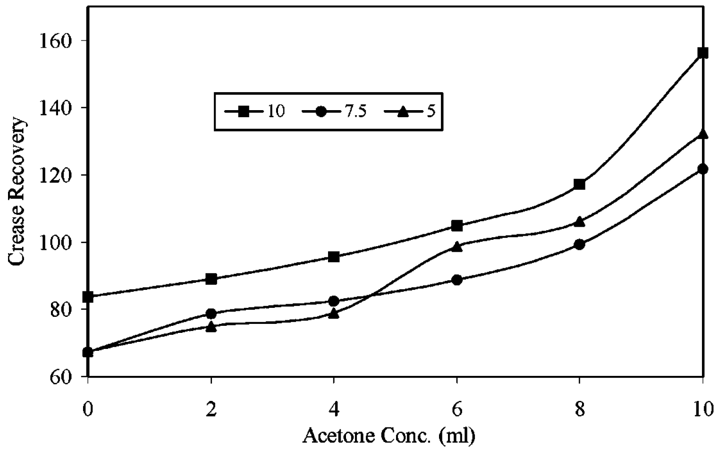

FIGURE 17 Crease recovery of cotton fabric modified using acetone.

with the concentration of the solvent. This may be attributed to the hydrolysis of the cyanoethyl group, which increases the crease recovery. Since the nitrile group shows poor recovery, the 0 ml of solvent shows less recovery than that of the solvent induced cyanoethylation. The graph seems to be similar for mlr5 also. Figure 20 shows that the acetone treated fabric shows a greater extent of recovery, which is due to the greater polarity of acetone.

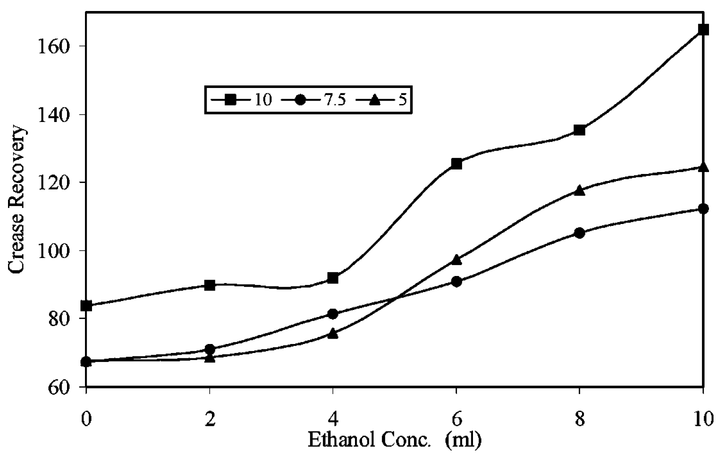

FIGURE 18 Crease recovery of cotton fabric modified using ethanol.

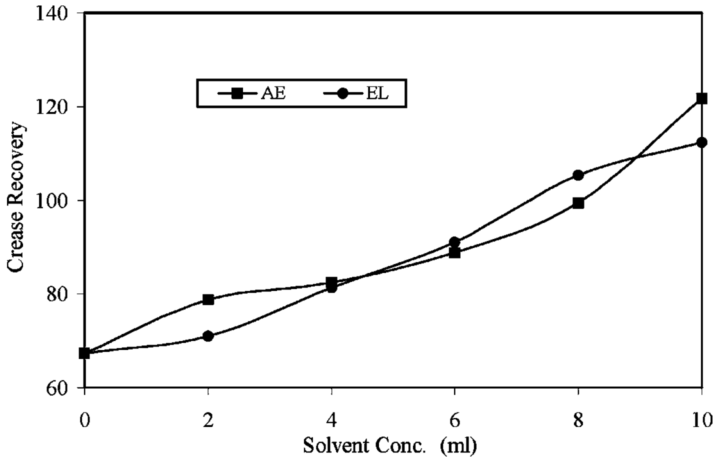

FIGURE 19 Crease recovery of solvent modified cotton fabric (mlr7.5).

Scanning Electron Microscopy

Scanning electron micrographs of mercerized, solvent induced cyanoethylation and hydroxylation were studied to observe the differences in surface morphology of the fibers. From the micrograph (Figure 21) it is noted that the fibers in mercerized cotton fabric are swollen and the surface appears to be uniform. In 0 ml of solvent the

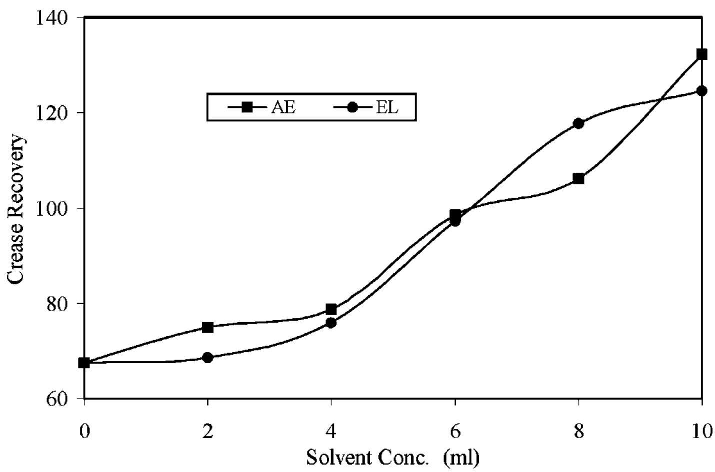

FIGURE 20 Crease recovery of solvent modified cotton fabric (mlr5).

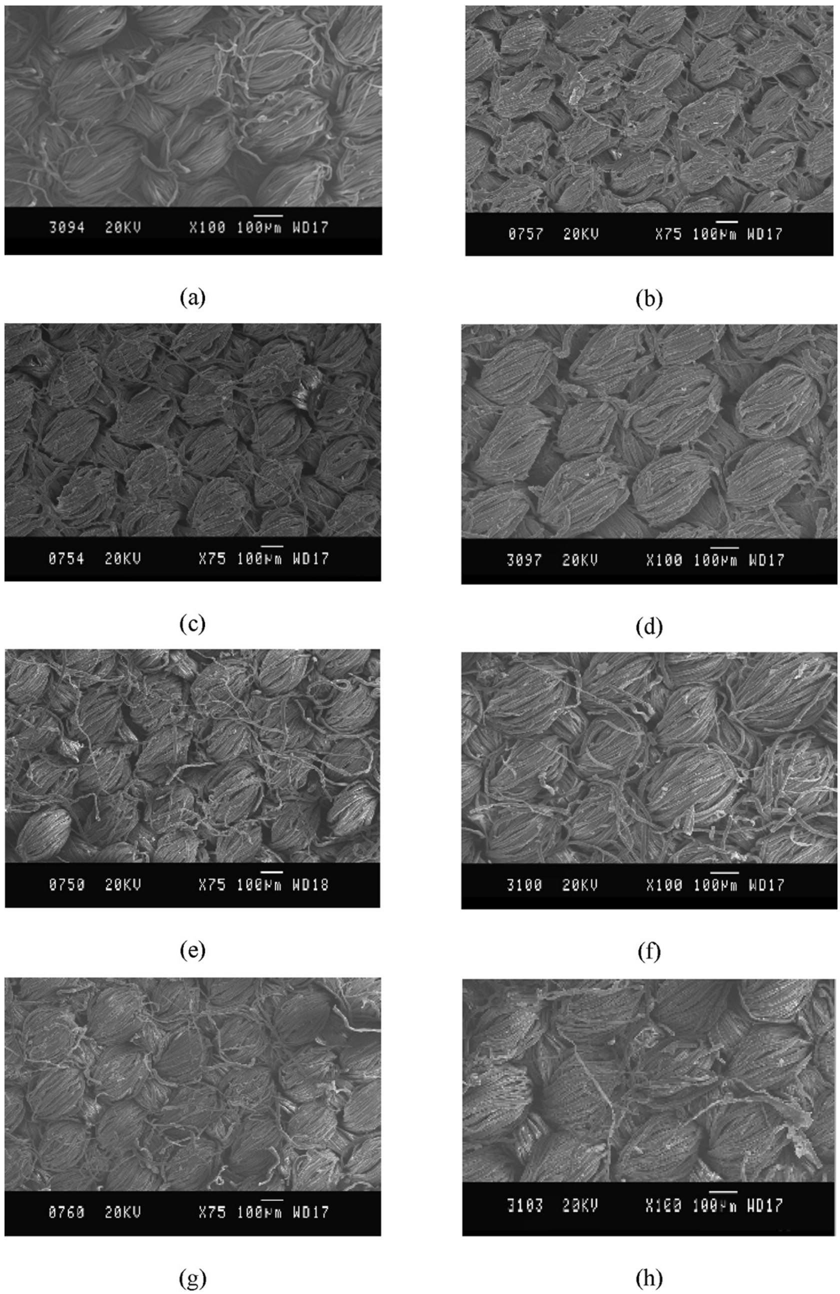

FIGURE 21 Scanning electron micrograph (a) mercerized (b) cyanoethylated (c) acetone 2 ml (d) ethanol 2 ml (e) acetone 8 ml (f) ethanol 8 ml (g) acetone 10 ml (h) ethanol 10 ml.

fibers show the formation of cyanoethyl groups, and coalesce with each other. The solvent induced cyanoethylated cotton fabric gives a proof for the hydrolysis of the cyanoethyl group. The fibers of acetone induced cyanoethylated cotton fabric appear to be greater in diameter than that of ethanol.

CONCLUSION

The shrinkage values of solvent treated samples of mlr10 are higher than the others. The shrinkage values are higher for samples treated with acetone than those of ethanol, which may be attributed to the greater polarity of acetone. The diameter of the yarn for different material to liquor ratio shows a similar trend. The percentage of nitrogen content and weight gain decrease with solvent concentration. With increased hydrolysis, the solvent treated samples show an improvement in crease recovery than that of cyanoethylated sample. Variation in properties with reduction in material to liquor ratio can be observed, which changes to a small extent. 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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