Effect of Solvent Induced Hydroxylation of Cyanoethyl Group on Dye Uptake of Cotton Fabrics

A. Selva Subha, S. Thambidurai

Department of Industrial Chemistry, Alagappa University, Karaikudi 630 003, Tamil Nadu, India

Received 7 February 2006; accepted 23 August 2006
DOI 10.1002/app.25784
Published online 23 January 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The present investigation deals with the dyeing behavior of solvent induced cyanoethylated cotton fabric. The modified cotton fabric was dyed by conventional method with commercial reactive dye (Drimarene Red). It is observed that acetone induced cyanoethylated samples exhibit higher color values than ethanol treated samples. The effect of nitrogen content on the dye uptake of modified fabric is assessed which shows a good correlation between them. It is obvious that crystallinity has a noticeable effect on the dye uptake of both solvent modified fabrics. For convenience and comparison, a set of samples are also dyed without addition of salt, alkali, and both. It is evident that even without addition of salt, alkali and both the samples exhibit a significant dye uptake. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1373–1377, 2008

Key words: cyanoethylation; reactive dye; dyeability; color strength

INTRODUCTION

With an aim of imparting new properties chemical modification of cellulose has been extensively studied. Previous studies have revealed that chemically modified cotton cellulose exhibits different behavior towards dyeing compared with that of unmodified cellulose. Hilw and Hebeish[1] investigated the effect of nature of the substituents of the modified cotton fabric on the susceptibility towards different dye stuffs.

Reactive dyes are most commonly employed because of their good color value and reasonably high fastness properties. It has been reported[2–7] that the cotton fabric is treated with various chemicals prior to dyeing to improve its dyeability with reactive dyes and to facilitate dyeing at neutral pH.[8,9]

In our earlier study[10] we have dealt with the effect of solvent-induced partial cyanoethylation and hydroxylation of cyanoethyl group on the physio-chemical properties of cotton fabric and found that hydroxylation of cyanoethyl group results in formation of amide group. Recently Bhattacharya and Agarwal[11] have reported the amide group formation on cellulose structure after polyacrylamide-hydrazine treatment on cotton and feasibility of neutral dyeing with reactive dyes.

Keeping this in mind, the present work aims to investigate the dyeability of solvent induced partially cyanoethylated cotton fabric using reactive dye and also the effect of solvent induced hydroxylation of cyanoethyl group on the dyeing behavior of cotton fabrics at neutral pH condition.

Correspondence to: S. Thambidurai (sthambi01@yahoo.co.in).

Journal of Applied Polymer Science, Vol. 108, 1373–1377 (2008)

EXPERIMENTAL

Materials and methods

Scoured plain weave cotton fabric (Area: 30 × 24 cm^2; Ends/in.: 140; Picks/in.: 80, Count: 40 s, Weight/sq. cm-0.015 g) was used throughout the study. All the chemicals used were laboratory grade. Surgical spirit was used for ethanol treatment. The dye sample (Drimarene Red HE3B) was supplied by Clariant dye manufactures.

Partial cyanoethylation

The solvent induced cyanoethylation using acetone and ethanol was carried out as described earlier.[10] The mercerised and acetone, ethanol induced modified cotton fabrics were dyed with Drimarene Red HE3B according to the conventional method using NaCl (30 gpl), sodium carbonate (15 gpl), 2% shade, and 1 : 20 liquor ratio. Dyeing temperature was raised from 40–80°C after which the dyeing was carried out for further 45 min. The dyed samples were taken out, washed with cold water, soaped at boil, rinsed thoroughly in hot water, washed again with cold water, and finally air-dried. The same method of dyeing was repeated without adding either salt or alkali and both. Mercerised sample was taken as control sample.

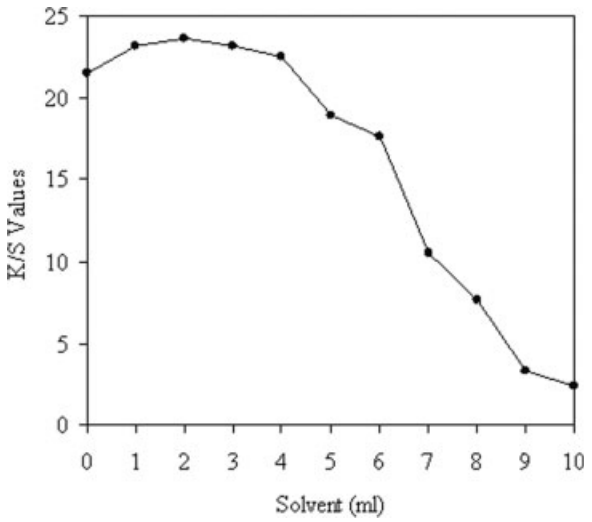

Figure 1 Effect of acetone concentration on *K/S* values.

Characterization and testing

Nitrogen content

Kjeldhal method[12,13] 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.[14] 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.[15]

Color measurement

The color values of the dyed fabrics were measured using spectrophotometer (Gretag Macbeth-2180 UV) Color iMatch according to the CIELAB color difference concept at standard illuminant D65/10° observer in the wavelength range of 360 to 750 nm at 10 nm intervals. The reflectance values were recorded at 2 points on each face of the folded fabric (8 points) at an interval of 1 cm from one point to the other.

RESULTS AND DISCUSSION

Effect of acetone

The *K/S* values of cyanoethylated cotton fabric in presence of acetone are depicted in Figure 1. The higher color strength of the modified cotton fabric than that of the control is due to the direct consequence of opening up of the cotton structure by the newly introduced cyanoethyl groups. At 0 mL of acetone the *K/S* value is 21.53, which is the value of fabric treated only with acrylonitrile. The introduction of acrylonitrile moieties in the form of cyanoethyl groups in the molecular structure of cotton enhances the dyeability significantly.[1] It is observed from the graph that the *K/S* values increases initially up to 4 mL of acetone. The increase in the *K/S* values by addition of acetone may be due to the formation of amide groups.[10,11] Further increase in acetone and decrease in acrylonitrile concentration the color strength decreases steadily. This may be due to the fact that with decrease in acrylonitrile concentration the formation of cyanoethyl group also decreases[16] and hence conversion of amide group.[10] At any concentration of acetone the *K/S* value is higher than that of control sample.

Effect of ethanol

Figure 2 shows the variation in dye uptake of the modified cotton fabric in presence of ethanol. It is apparent from the graph that *K/S* value decreases significantly up to 4 mL of ethanol after that it tends to level off at higher concentration. In the ethanol induced partial cyanoethylation, when the alkali swollen cotton fabric is introduced into the reaction mixture at room temperature the bath temperature increases to 60–65°C and hence it is expected that some by-product might have also been formed during this reaction which results in poor substitution reactions. These factors may account for the poor color values in the case of ethanol modified samples. The decrease in *K/S* value can also be interpreted by increase in crystallinity produced by the ethanol treatment.[10]

Effect of nitrogen content

Figure 3 illustrates the variation of dye uptake with nitrogen content of the modified cotton fabric using

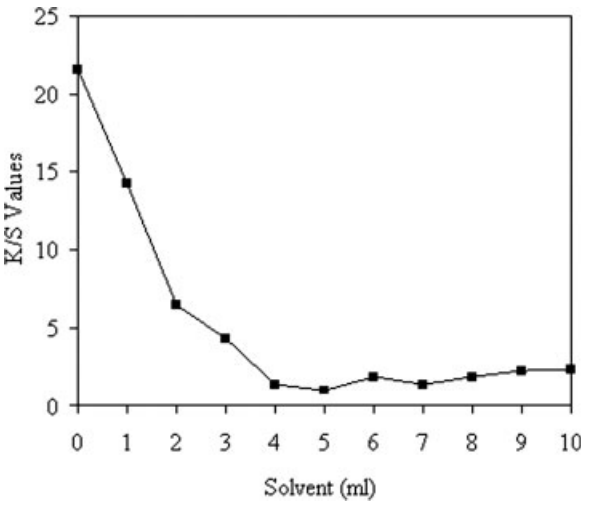

Figure 2 Effect of ethanol concentration on *K/S* values.

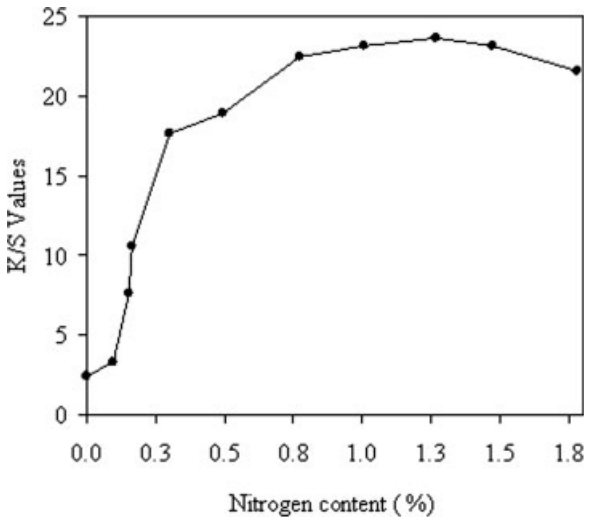

Figure 3 Relationship between nitrogen content and dye uptake of acetone modified samples.

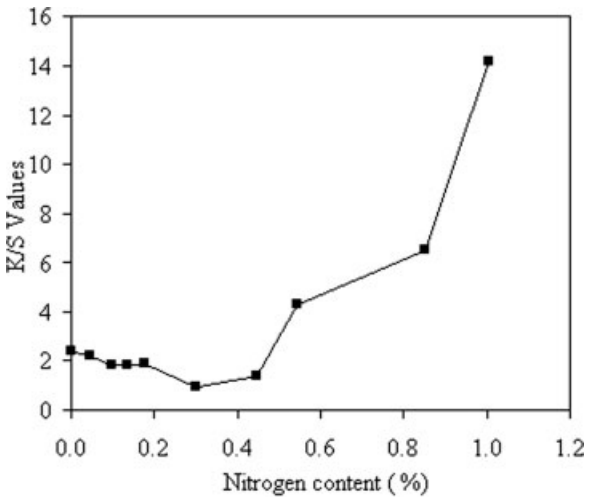

Figure 4 Relationship between nitrogen content and dye uptake of ethanol modified samples.

acetone as solvent. It is apparent from the graph that with increase in nitrogen content *K/S* value show a sudden increase up to 0.8% of nitrogen content and then a gradual increase is noted. At higher percentage of nitrogen content (1.8%) a slight fall is observed. This can be explained by the fact that higher substitution can lead to two mutually opposing effects *viz*., increase in distention, which can cause an increase in dye uptake. Another effect is the blocking of more and more OH groups resulting in few hydroxyls available for binding with the dye that ultimately can lead to a reduction in dye uptake.[17] The slight increase in dye uptake between 0.8–1.5% of nitrogen content may be due to the formation of solvent induced amide groups[10] and decrease is due to the absence of amide group.

The effect of degree of cyanoethylation of cotton fabric (Percentage of nitrogen content) on dye uptake of ethanol modified cotton fabric (CE) is shown in Figure 4. The plot reveals that as the nitrogen content increases the dye uptake also increases. The trend shows the same level of dye uptake, which is followed up to 0.4% nitrogen content, and then a steady increase is observed in the curve. This may also be attributed to that with an increase in degree of cyanoethylation the dye fixation also increases significantly.[16]

Infrared index

The crystallinity of the cotton fabric was decreased by alkali and acrylonitrile treatment when compared to that of the counter part (Table I). Hirai et al.[18] showed that the crystallinity could be decreased by the cyanoethylation treatment. These results could be attributed to the larger volume of the cyanoethyl group by virtue of which it is able to bring about more severe distension of molecular bundles.[17] The infrared index of 0 mL of acetone induced cyanoethylated fabric is higher than the infrared index obtained for 2 mL which may be the reason for increase in color value. As is evident increasing the cyanoethyl content is accompanied by a substantial reduction in the dye uptake, a point which supports the above findings.[19]

The *K/S* values are plotted against the IR index of the acetone modified cotton fabric which is shown in Figure 5. It is apparent from the graph that with increase in infrared index the *K/S* value decreases steadily. The results also show that at lower values of infrared index a higher decrystallizing effect is noted than the others. A good correlation is observed between IR index and *K/S* values.

It is obvious from the Figure 6 that for ethanol treated fabrics the curve decreases from the beginning and then it tends to level off. In general, while comparing the acetone and ethanol treatment, the dye uptake is more for former one than that of latter. This can be explained by the fact that greater polarity of the solvent increases the color yield to a greater extent.

From the above analysis, it is evident that the *K/S* values of ethanol induced cyanoethylated samples are found to be very low and for acetone modified

TABLE I
Infrared Index and *K/S* Values of Modified Cotton Fabric

	Acetone		Ethanol	
Solvent concentration (mL)	Infrared index	*K/S* value	Infrared index	*K/S* value
Mercerized	0.714	1.83	0.714	1.83
0	0.416	21.53	0.416	21.53
2	0.284	23.60	0.205	6.51
4	0.319	22.48	0.240	1.36
6	0.388	17.60	0.300	1.90
8	0.454	7.68	0.333	1.82
10	0.600	2.41	0.400	2.40

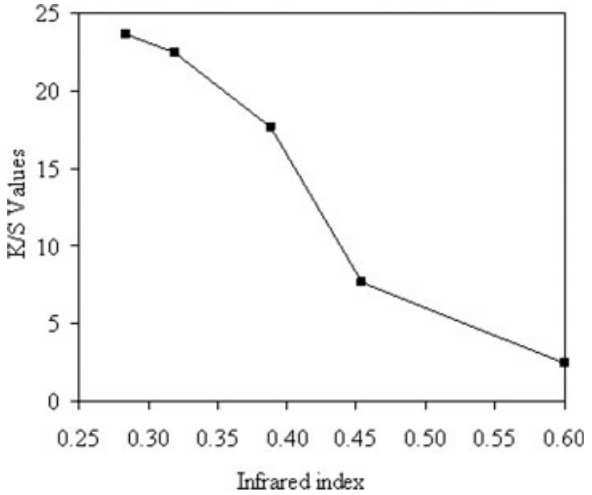

Figure 5 Relationship between infrared index and dye uptake of acetone modified samples.

cotton fabrics it is higher at lower concentration of acetone (Table I). Hence, the effect of hydroxylation of cyanoethyl group on dye uptake in the absence of salt, alkali, and both was dealt only for the acetone treated samples (up to 5 mL). A comparison of *K/S* values of these samples along with the conventionally dyed samples are depicted in Figure 7.

In conventional dyeing the *K/S* value gradually increases, and with further addition of acetone the curve falls suddenly. This is in accord with the findings of Hilw and Hebeish[1] in which they have reported that the fabric treated with 100% acrylonitrile shows a less in color strength than that of the 50 : 50 and 25 : 75 of acrylonitrile: water by volume. The same trend was observed for the no alkali treatment but there is slight reduction in color strength of the fabric. Even though no alkali is present in the dye bath, modified fabrics show a significant uptake which may be because of the presence of amide group.

But in the case of no salt, the exhaustion may be low and hence, it shows lower dye uptake than that

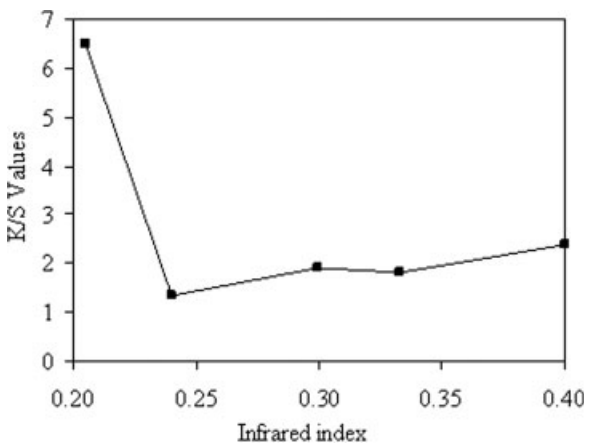

Figure 6 Relationship between infrared index and dye uptake of ethanol modified samples.

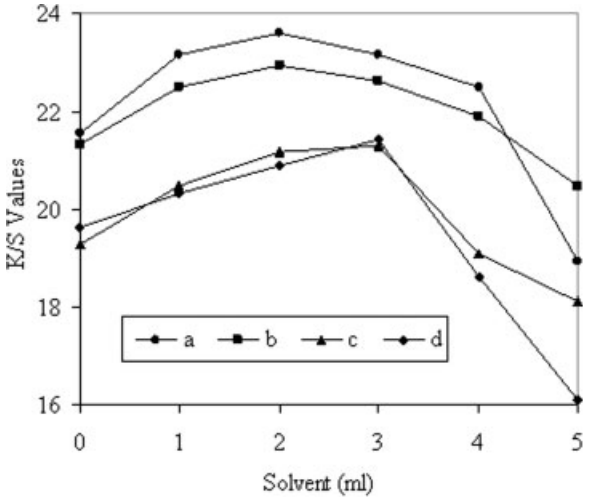

Figure 7 Color strength of acetone modified cotton samples (a) Conventional (b) No alkali (c) No salt (d) No salt and alkali.

of no alkali treated samples. The results obtained show an increment in the *K/S* values up to 3 mL of acetone concentration and then the curve drops. The no salt and alkali samples show an increase in the curve and further increase in acetone concentration causes the *K/S* values to decrease. In no salt and alkali dyeing, remarkable color strength is noted. This may be attributed to the presence of amide group in the modified fabric. The trend for no salt, no salt and alkali samples are almost similar to each other but the no salt samples show a greater enhancement in dye uptake than that of no salt and alkali at higher acetone concentration.

It is also evident that even without addition of salt, alkali and both a significant dye uptake is observed in the modified samples. The color strength of no salt, no alkali, no salt and alkali samples are higher than that of the control but a slight reduction is observed when compared to conventionally dyed samples. The decrease in dye uptake after 4 mL may be attributed to the lower substitution and hence less hydrolysis of the nitrile to amide group.[10] On comparing all the dyed samples, the color strength values follow the order: conventional > no alkali > no salt > no salt and alkali.

CONCLUSIONS

The dyeability using reactive dye for the modified cottons showed that the *K/S* values (color strength) depend on the degree of substitution as well as the micro structural changes of the cotton cellulose caused by chemical modification.

In conventionally acetone induced cyanoethylated samples, the dye uptake increases initially and then decreases gradually. On the other hand, conventionally ethanol induced cyanoethylated samples displays a decrease in the color strength and then levels off.

The effect of ethanol concentration on dye uptake properties is very low. The correlation between *K/S* values and percentage of nitrogen content suggests that increase in nitrogen content enhances the dye uptake of the modified fabric. The IR index of the modified fabric gives proof for the enhancement in the dyeability. On comparing with other three methods of dyeing, the samples dyed with no salt and alkali shows a marginal reduction in dye uptake value up to 3 mL of acetone concentration. It may be concluded that at neutral pH condition more or less same color value can be obtained with the addition of low acetone concentration in the mixture of partial cyanoethylation of cotton cellulose.

The authors are grateful to Dr.T.Vasudevan, Professor and Head, Department of Industrial Chemistry for aiding fruitful suggestions and constant inspiration to finish the work.

References

1. El-Hilw, Z. H.; Hebeish, A. J Soc Dyers Color, 1999, 118, 220.
2. Soignet, D.; Berni, G.; Benerilo, R. Text Res J 1966, 36, 978.
3. Hebeish. Am Dyest Rep 1986, 75, 22.
4. Hebeish, El-Rafie, M. H. Am Dyest Rep 1990, 79, 34.
5. Hamza, H. M.; El-Nabas, H. M. J Soc Dyers Colour 1991, 107, 144.
6. Rupin, M. Text Chem Color 1976, 8, 139.
7. Evans, G. E.; Shore, J.; Stead, C. V. J Soc Dyers Colour 1984, 100, 304.
8. Burkinshaw, S. M.; Lei, X. P.; Lewis, D. M. J Soc Dyers Colour 1989, 105, 391.
9. Burkinshaw, S. M.; Lei, X. P.; Lewis, D. M. J Soc Dyers Colour 1990, 106, 307.
10. Subha, A. S.; Thambidurai, S. J Appl Polym Sci, to appear.
11. Bhattacharya, S.; Agarwal, B. J. Indian J Fiber Text Res 2003, 28, 332.
12. Trotman, S. R.; Trotman, E. R. In Textile Analysis, Charles Griffin: London, 1948, p 62.
13. Alvasker, J.; Turner, H. A. J Soc Dyers Colour 1955, 71, 797.
14. O'Connor, R. T.; Durpe, E. F.; McCall, E. R. Anal Chem 1957, 29, 998.
15. Nelson, M. L.; O'Connor, R. T. J Appl Polym Sci 1964, 8, 1325.
16. Kamel, M.; Hebeish, A.; Moursi, A. Z. J Soc Dyers Color 1974, 90, 352.
17. Bhama Iyer, P.; Krishna Iyer, K. R.; Patil, N. B.; Bhatt, I. G. J Appl Polym Sci, 1980, 25, 2235.
18. Hirai, A.; Tsuji, W.; Kitamaru, R.; Masao, H. J Appl Polym Sci 1976, 20, 3365.
19. Hebeish, A.; Moursi, A. Z.; Khalil, M. I.; Abdel- Mohdy, F. A. J Appl Polym Sci 1977, 21, 2191.