Modification of Cellulose Acetate Fabric with Cyclodextrin to Improve Its Dyeability

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ABSTRACT: Cellulose acetate fibers are usually dyed with disperse dyes in the presence of various additives to ensure coloration leveling. The possibilities of formation of complexes between disperse dye molecules and cyclodextrin (CD) can be of beneficial use. In this respect, the modification of the fiber with CD, then subjecting it to dyeing with disperse dye was performed on the basis of host/guest system as an alternative to overcome the low solubility of disperse dyes in water. The additives of the dyeing bath can be eliminated. The attained color intensities as well as the fastness properties are enhanced upon using CD. The depth of the dye inside the fiber structure is highly enhanced, while the thermal properties such as the glass transition temperature, crystallinity temperature, and melting temperature remain nearly constant. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3192–3198, 2009

Key words: cellulose acetate; cyclodextrin; dyeing; disperse dye; differential thermal analysis; glass transition temperature; modification

INTRODUCTION

Cellulose acetate (CA) fibers are usually dyed with disperse dyes. Additives play an important role in the dyebath to enhance the dye solubility via the ability to form dispersion system. Dyeing of CA fibers by the methods used for cellulosic fibers is difficult because of the saponification possibility of the acetyl groups.[1] Indirect evidences for the implication of plasticization and swelling phenomena on dyeing of CA fibers are proved by the relative facility of diffusion of the dye molecules into preswelled fibers.[2,3] The dyeing behavior of CA fibers is very similar to that of synthetic fibers, particularly with respect to its affinity to water-insoluble dyes.[4] The dye affinity of CA fibers increases by the increase of the amount of bound modified groups.[2]

In dyeing processes, the use of cyclodextrin (CD) can improve the uptake of disperse dyes by polyester fibers because CD increases the tendency of disperse dye solubilization in aqueous solutions.[5]

CD is characterized by a hydrophobic internal cavity and by a hydrophilic exterior. This can give different inclusions of dye molecules depending on the size of the cavity.[6–9] The formation of complexes between the dye molecules and CD has been thoroughly described and can be used as an alternative to dyebath additives.[5,10–15] The structure of CD shows an ability of inclusion of complexes with compounds having a molecular size complementary to the cavity dimensions.[16] No covalent bond is established between the dye molecules as a guest in the CD host molecules. Consequently, the dissociation–association equilibrium in solution becomes one of the characteristic features of the guest/host association. One of the modification possibilities of the fiber surface to alter its properties is attained by a successful binding of CD to the fibers.[13,17,18]

It is aimed in this work to perform a systematic investigation on pretreatment of CA with CD through variation of the treatment conditions namely, concentration of CD and the thermofixation temperature. The changes induced in the fibers dyeing properties are evaluated through measurements of the color intensity, dye uptake, fastness properties, as well as the depth of dye molecules penetration inside the fiber structure. Thermal behavior of pretreated CA is also tried.

EXPERIMENTAL

Materials

White secondary CA, satin weave, of density 1.32 g/cm^3 and of 38.5% acetyl content was used. The fabric was precleansed in an aqueous solution containing 3 g/L of a weakly cationic detergent, 2 mL/L ammonia solution (25%) at 65°C for 20 min followed by warm and cold rinsing. The fabric was dried under ambient conditions.

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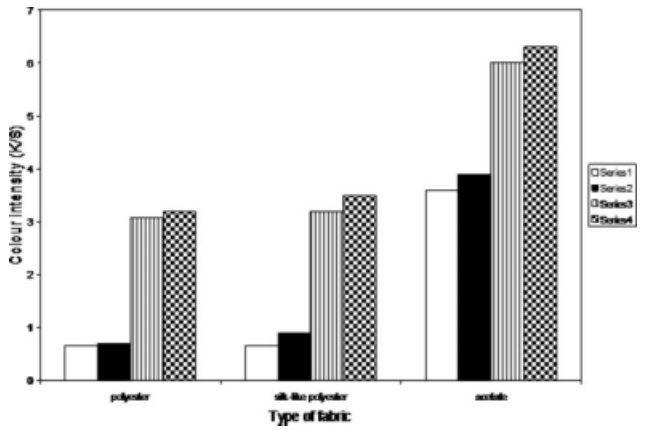

Figure 1 Effect of adding CD into the dyebath on the dyeability of different fibers at different dyeing temperatures. Dyeing: 1% C. I. Disperse Red 60, 1% (v/v) CD, pH 4.5, liq ratio 1 : 50. Series 1: dyed at 85°C without CD, series 2: dyed at 85°C with CD, series 3: dyed at 100°C without CD, and series 4: dyed at 100°C with CD.

Chemicals and reagents of pure grade were used in this study namely, β-cyclodextrin and monochlorotriaznyl-β-cyclodextrin Na-salt (MCT-CD). Commercial disperse dyes such as C. I. Disperse Red 60 (anthraquinone structure) and C. I. Disperse Red 82 (monoazo structure) were used.

Treatments

CA samples of known weight were treated with both CD and MCT-CD by a padding technique. The samples were soaked in a solution containing CD of concentration (0.1–1.5 g/100 g fiber) at room temperature (~ 25°C), followed by squeezing under pressing rollers to 100% pick up. The samples were then thermofixed at temperatures varied from 120–150°C for 3 min. The samples were then subjected to the dyeing process. Other samples were dyed after padding without thermofixation. Another treatment technique was tried by adding CD directly to the dyebath as an additive during the dyeing process.

Dyeing procedure

CA samples of known weights were exhaust dyed in a dyebath at different temperatures (60–80°C) for various time intervals (10–120 min). The dyeing solution was adjusted to pH 5.5 by adding acetic acid. The dyed CA fabric was warm and cold rinsed with soap solution. The samples were then rinsed thoroughly with water and air dried at room temperature. Two different structural dye moieties (anthraquinone and monoazo) were applied in this investigation. The dyeing of the CD-pretreated CA fiber is carried out when compared with the untreated one, meanwhile maintaining the dyestuff and the dyeing conditions unchanged.

Color measurement

The spectral reflectance measurements of the dyed fabric were carried out using a recording filter spectrophotometer (model ICS Texicon, Kennetside Park Newbarge, Berkshire AG 145TE, UK). The color intensity expressed as K/S values of the dyed samples was determined by applying the Kubelka-Munk equation:

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_o)^2}{2R_o},$$

where R is the decimal fraction of the reflectance of the dyed sample, R_o is the decimal fraction of the reflectance of the undyed sample. K is the absorption coefficient and S is the scattering coefficient.[19]

The relative color intensity is estimated by applying the following equation:

$$\text{The relative color intensity \%} = \frac{K/S \text{ of pretreated sample}}{K/S \text{ of untreated sample}} \times 100$$

Color fastness

The color fastness to crocking and washing was measured according to the AATCC test method 8, 1972 and test method 83-1974, respectively.[20] Evaluation of the washing fastness was given using the Gray Scale reference for color change.

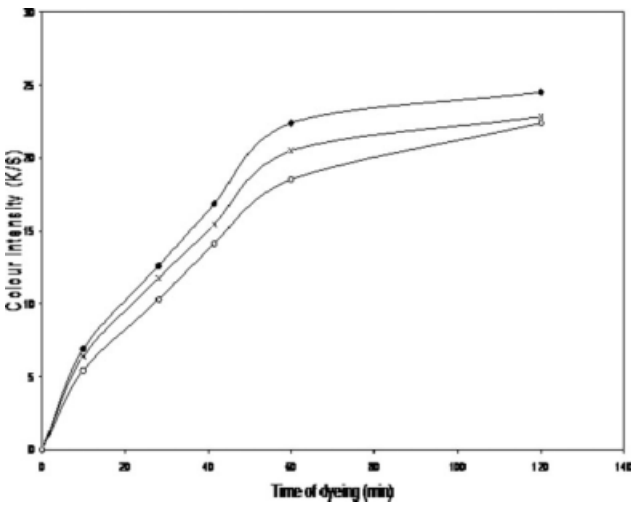

Figure 2 Dependence of the dyeability on the time of dyeing of CA fabric pretreated with CD or MCT-CD. Treatment: padding, pick up 100%, 0.2 g/100 g fiber, thermofixation at 150°C, 3 min, pH 8.0, ○-○ treated with MCT-CD, x-x untreated, •-• treated with CD. Dyeing: 1% (o.w.f.) C.I. Disperse Red 82, 80°C, pH 5.5, liq. ratio 1 : 50.

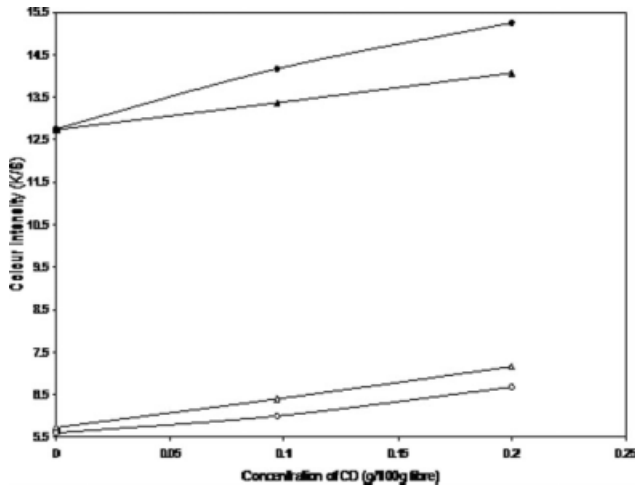

Figure 3 Effect of CD concentration on dyeability of pretreated CA fabric. Treatment: padding, pick up 100%, pH 8.0, thermofixation at 150°C, 3 min. Dyeing: 0.5% (o.w.f.) C.I. Disperse Red 82, 80°C, pH 5.5, liq. ratio 1 : 50, △-△ pretreated acetate thermofixed and dyed for 10 min, ○-○ pretreated acetate without thermofixation and dyed for 10 min, •-• pretreated acetate thermofixed and dyed for 30 min, ▲-▲ pretreated acetate without thermofixation and dyed for 30 min.

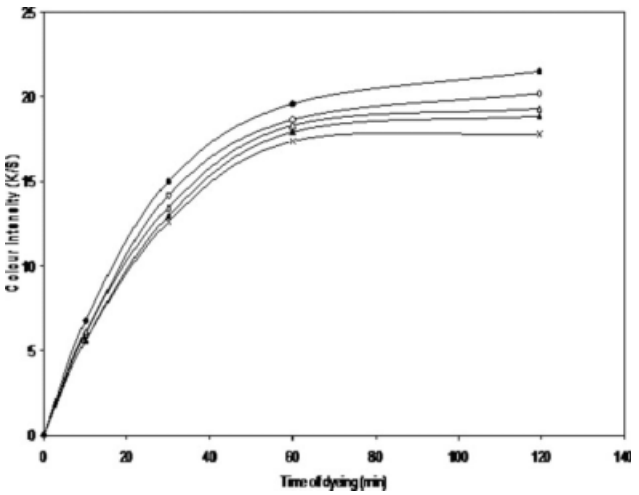

Figure 5 Effect of time of dyeing on the color intensity of the dyed CA fabric pretreated with various concentrations of CD. Treatment: padding, pick up 100%, pH 8.0, thermofixation at 150°C, 3 min, x-x untreated, ○-○ 0.1 g CD/100 g fiber, •-• 0.2 g CD/100 g fiber, △-△ 1 g CD/100 g fiber, ▲-▲1.5 g CD/100 g fiber. Dyeing: 0.5% (o.w.f.) C.I. Disperse Red 82, 80°C, pH 5.5, liq. ratio 1 : 50.

Characterization

The differential thermal analysis of CA samples was carried out using the thermal analyzer 7 series (Perkin–Elmer, Boston, MA)

Scanning electron microscopy of CA samples was performed to study the changes induced in surface properties of pretreated CA fabric. The dyed samples were subjected to microscopic analysis to record the extent of dye penetration into the interior of the fiber structure.

RESULTS AND DISCUSSION

A systematic study on the influence of CD treatments on the dyeing of CA fabric with disperse dye was performed to optimize new possibilities to dye CA fabric at a lower temperature than the conventional dyeing one without using additives as well as enhancing the fastness properties and increasing the dye penetration into the interior of the fiber structure to ensure homogeneity and leveling of the dye.

Disperse dyes are hydrophobic compounds, it was anticipated that CD could serve as host sites if

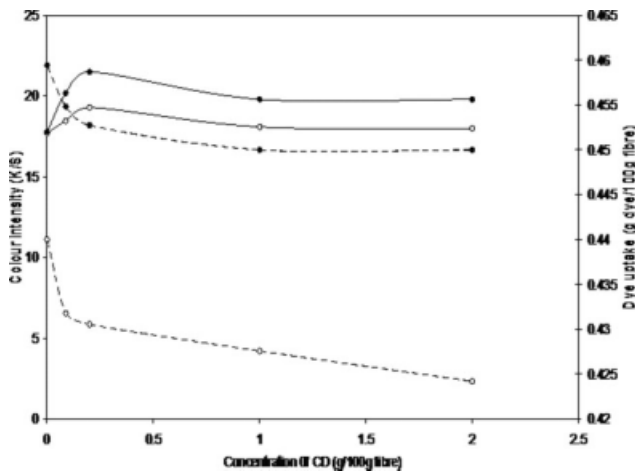

Figure 4 Dependence of the color intensity of the dyed pretreated CA fabric and its dye uptake on the concentrations of CD. Treatment: padding, pick up 100%, pH 8.0, thermofixation at 150°C, 3 min. Dyeing: 0.5% (o.w.f.) C.I. Disperse Red 82, 80°C, pH 5.5, liq. ratio 1 : 50, ○-○ 60 min, •-• 120 min, ____ color intensity, _ _ _ dye uptake.

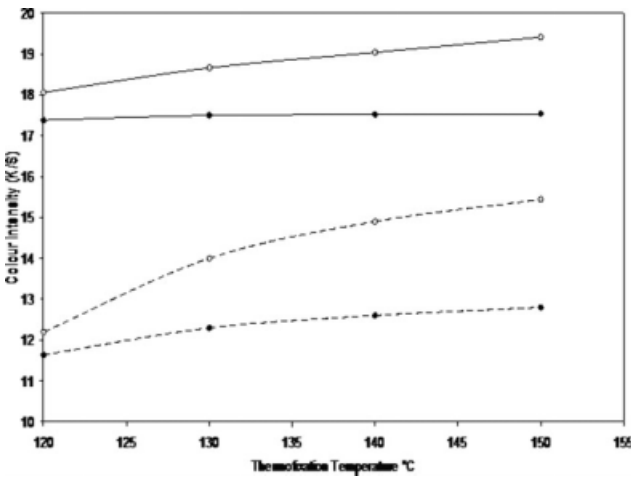

Figure 6 Dependence of the acquired color intensity of the dyed CA fabric pretreated with CD on the thermofixation temperature. Treatment: padding, pick up 100%, 0.2 g CD/100 g fiber, pH 8.0, 3 min, •-• untreated acetate, ○-○ treated acetate. Dyeing: C.I. Disperse Red 82, 80°C, 45 min, pH 5.5, liq. ratio 1 : 20, _ _ _ 0.5% (o.w.f.), _____ 1% (o.w.f).

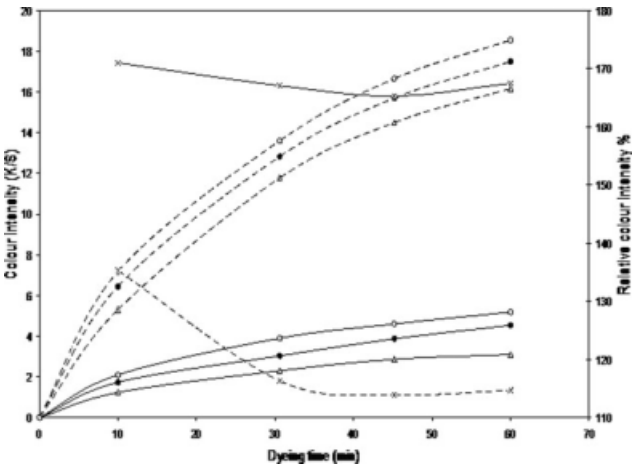

Figure 7 Dependence of the acquired color intensity of the dyed CA fabric pretreated with CD on the dyeing time. Treatment: padding, pick up 100%, 0.2 g CD/100 g fiber, pH 8.0, 3 min, △-△ untreated, •-• thermofixed at 130°C, ○-○ thermofixed at 150°C. Dyeing: 80°C, pH 5.5, liq. ratio 1 : 50, _ _ 1% (o.w.f.) C.I. Disperse Red 82, ___ 0.5% (o.w.f) C.I. Disperse Red 60, x-x relative color intensity for pretreated acetate at 150°C.

incorporated into the molecular structure of a warp size.[13,21] Dyeing with disperse dye in the presence of CD in the dye bath was carried out on polyester, silk-like polyester, and CA fabrics at 85 and ~ 100°C. The results are shown in Figure 1. Presence of CD in the dyebath enhances the color intensity of the examined fabrics. The CA and the silk-like polyester fabrics were mostly colored at lower dyeing temperature. The study is therefore confined to CA fabric.

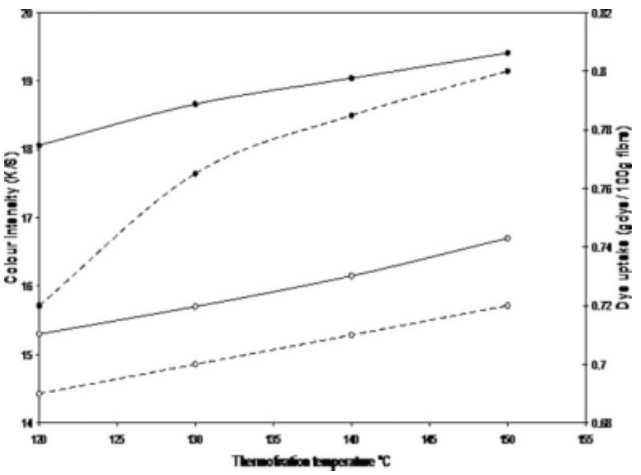

Figure 8 Dyeability of pretreated CA fabric with CD at different temperatures in relation to the liquor ratio. Treatment: padding, pick up 100%, 0.2 g CD/100 g fiber, pH 8.0, 3 min. Dyeing: 1% (o.w.f.) C.I. Disperse Red 82, 80°C, 45 min., pH 5.5, •-• liq. ratio 1 : 20, ○-○ liq. ratio 1 : 50, _ _ dye uptake, ___ color intensity.

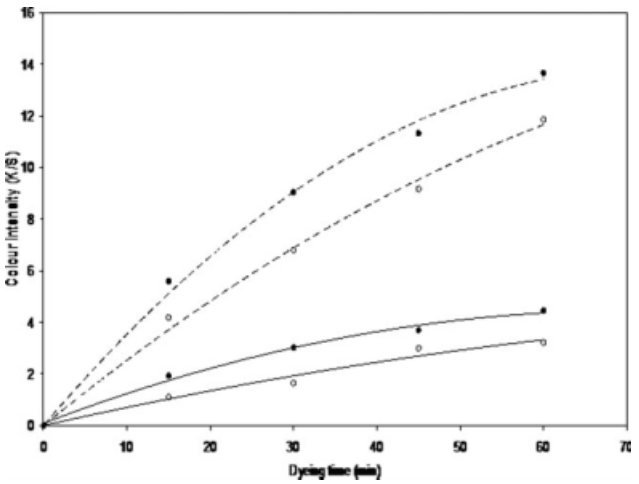

Figure 9 Dependence of the color intensity of the dyed CD-treated CA fabric on the dyeing time at different temperatures. Treatment: 0.2 g CD/100 g fiber, padding, pick up 100%, pH 8.0, 150°C, 3 min, ○-○ untreated CA, •-• treated CA. Dyeing: 0.5% (o.w.f.) C.I. Disperse Red 82, pH 5.5, liq. ratio 1 : 50, _ _70°C, ___ 60°C.

Treatment with CD and MCT-CD

CA fabric was treated with CD and MCT-CD by padding technique and then thermofixed at 150°C for 3 min. The effect of these treatments on the dyeability of CA fabric with disperse dye is shown in Figure 2. CD treatment offered a significant dyeability effect on CA than MCT-CD.

Effect of CD concentration

The effect of CD concentration on the dyeability of pretreated CA fabric is illustrated in Figures 3–5. The color intensity of the dyed CA fabric pretreated with various concentrations of CD is shown in Figure 3. It can be noticed that the color intensity of the dyed CA was found to depend on the CD concentration and increased with increasing CD concentration up till 0.2 g/100 g fiber. It can be also noticed that the CD treatment followed by thermofixation imparted an improvement in the dyeability of CA fabric more than the treatment without thermofixation (Fig. 3).

Figure 4 represents the dependence of both the dye uptake and the acquired color intensity on the concentration of CD. The dyeing was performed for

TABLE I
Differential Thermal Analysis of Untreated and Pretreated CA Fabric with CD

CA Sample	T_g (°C)	T_c (°C)	T_m (°C)
Untreated	64.5	168.8	260
Pretreated with CD	62.1	163.0	259

Treatment: padding, pick up 100%, 0.2 g CD/100 g fiber, pH 8.0, 150°C, 3 min.

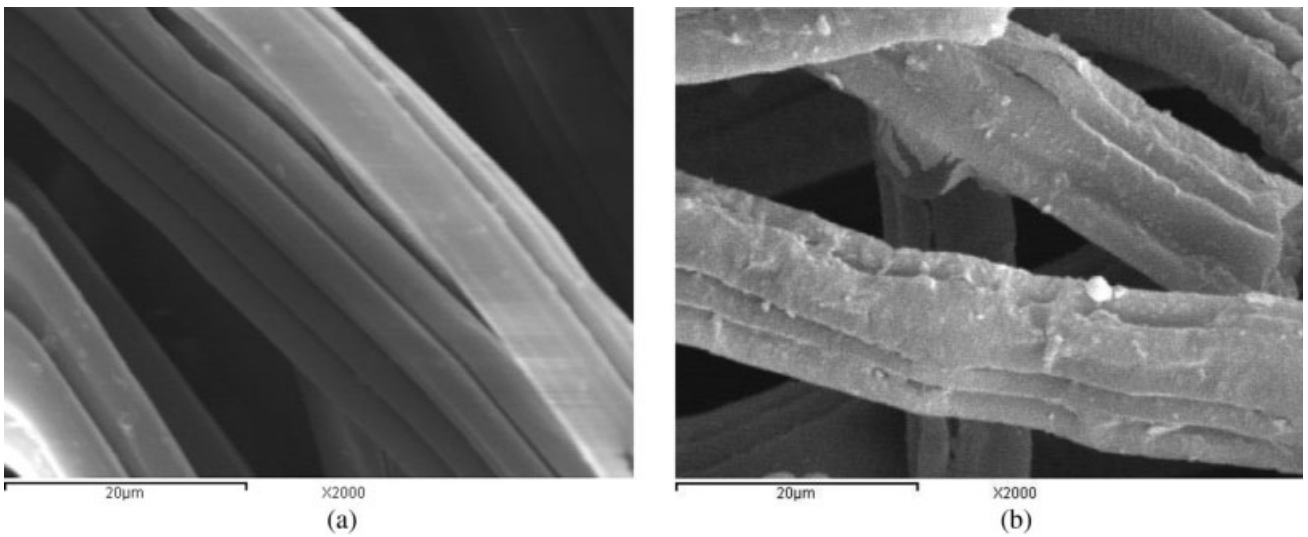

Figure 10 (a) SEM of untreated CA fabric. (b) SEM of treated CA fabric with CD. Treatment: padding, pick up 100%, 0.2 g CD/100 g fiber, pH 8.0, 150°C, 3 min.

60 and 120 min to study the effect of CD treatment at longer dyeing time. It was found that the color intensity of the dyed pretreated CA had increased preferentially.

The dependence of color intensity of the dyed CA pretreated with various concentrations of CD on the time of dyeing is illustrated in Figure 5. The CA dyeing process was found to be time- and CD concentration-dependent.

Effect of thermofixation temperature

The effect of thermofixation temperature on the dyeability of pretreated CA fabric is given in Figures 6–8. The dependence of color intensity of the dyed pretreated CA fabric on the thermofixation temperature is represented in Figure 6. There is a noticeable improvement in the dyeability of pretreated CA at the two applied shades (0.5 and 1%), and the acquired color intensity was found to increase with increasing the thermofixation temperature. It can also be noticed that the treatment attained good effect at the lower shade (Fig. 6). Figure 7 shows that the color intensity increased with increasing the dyeing time as well as the applied shade, whereas the relative color intensity behaved oppositely. The relative color intensity of the pretreated CA dyed with 0.5% C. I. Disperse Red 60 (based on anthraquinone) is higher than that dyed with C. I. Disperse Red 82 (based on monoazo). C. I. Disperse Red 60 is characterized as medium energy levels disperse dye; compactness of anthraquinone moiety affords rapid penetration, whereas the monoazo moiety attains a higher energy level for dyeing and large molecular volume.[22] Hence, the dye uptake of the former by CA fabric seems to be higher than the other one. The effect of liquor ratio on both the dye uptake and the acquired color intensity at various thermofixation temperatures is shown in Figure 8. The lower liquor ratio the higher is the dye uptake. This may reflects on the possibility of saving energy and water consumption in the dyeing process of the CA fabric.

Dyeing temperature

Dyeing of CA fabric pretreated with CD at dyeing temperatures of 60 and 70°C was tried, and the dependence of the acquired color intensity on the dyeing time is shown in Figure 9. It can be concluded that CD treatment of CA fabric then dyed can afford a color intensity at dyeing temperature of 70°C, having good leveling comparable to that attained on untreated CA dyed at 80°C, using the monoazo C. I. Disperse Red 82 (Figs. 6 and 9).

Differential thermal analysis

The differential thermal analysis data of the untreated CA and that one pretreated with CD is given in Table I. A slight decrease in glass transition

TABLE II
Diameter and Depth of Dye in Cross- and Longitudinal Section of Untreated and Pretreated Acetate Fabric with CD

CA sample	Mean diameter (µm)	Mean dye depth (µm)	
		Cross section	Longitudinal section
Untreated	10.23	1.09	0.99
Pretreated with CD	7.05	2.6	2.1

Treatment: padding, pick up 100%, 0.2 g CD/100 g fiber, pH 8.0, 150°C, 3 min.

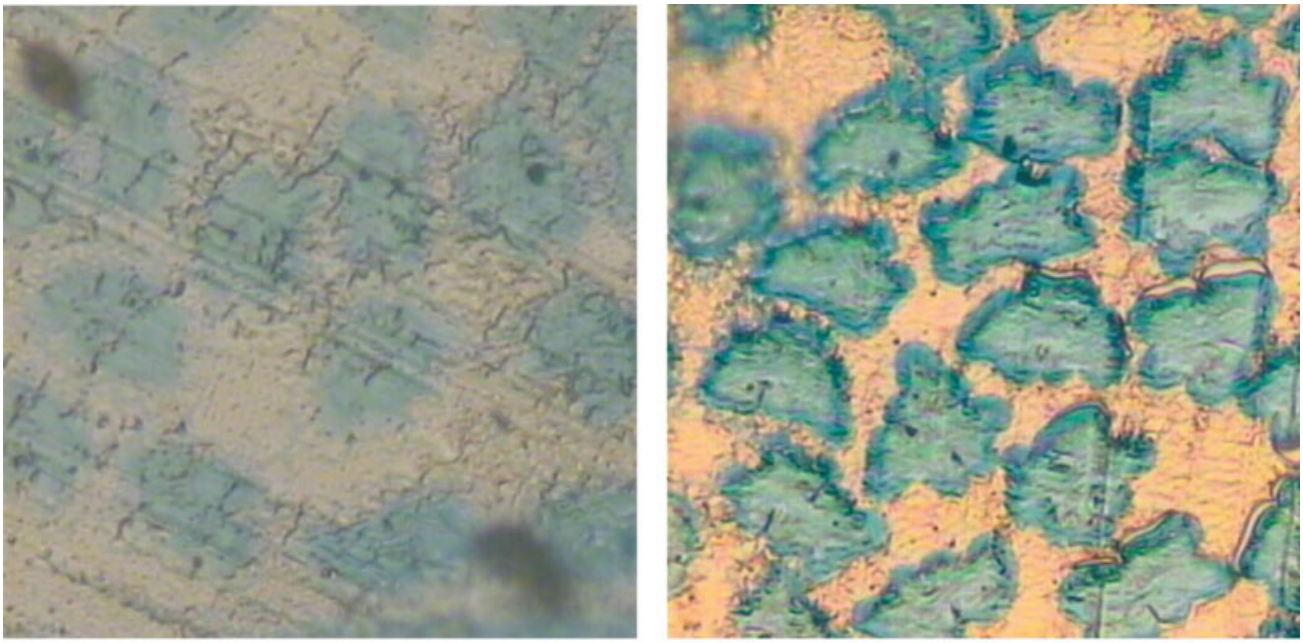

Figure 11 (a) Cross section of untreated dyed CA fabric. Dyeing: 1% (o.w.f.) C.I. Disperse Red 82, 80°C,1 h, pH 5.5, liq. ratio 1 : 50. (b) Cross section of pretreated dyed CA fabric. Treatment: padding, pick up 100%, 0.2 g CD/100 g fiber, pH 8.0, 150°C, 3 min. Dyeing: 1% (o.w.f.) C.I. Disperse Red 82, 80°C,1 h, pH 5.5, liq. ratio 1 : 50. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature (T_g), crystallinity temperature (T_c), and melting temperature (T_m) was observed. CD treatment of CA fabric imparts no effect on the thermal properties of CA.

Microscopic analysis

Scanning electron micrographs (SEM) of the untreated and pretreated CA fabric with 0.2 g CD/100 g fiber,

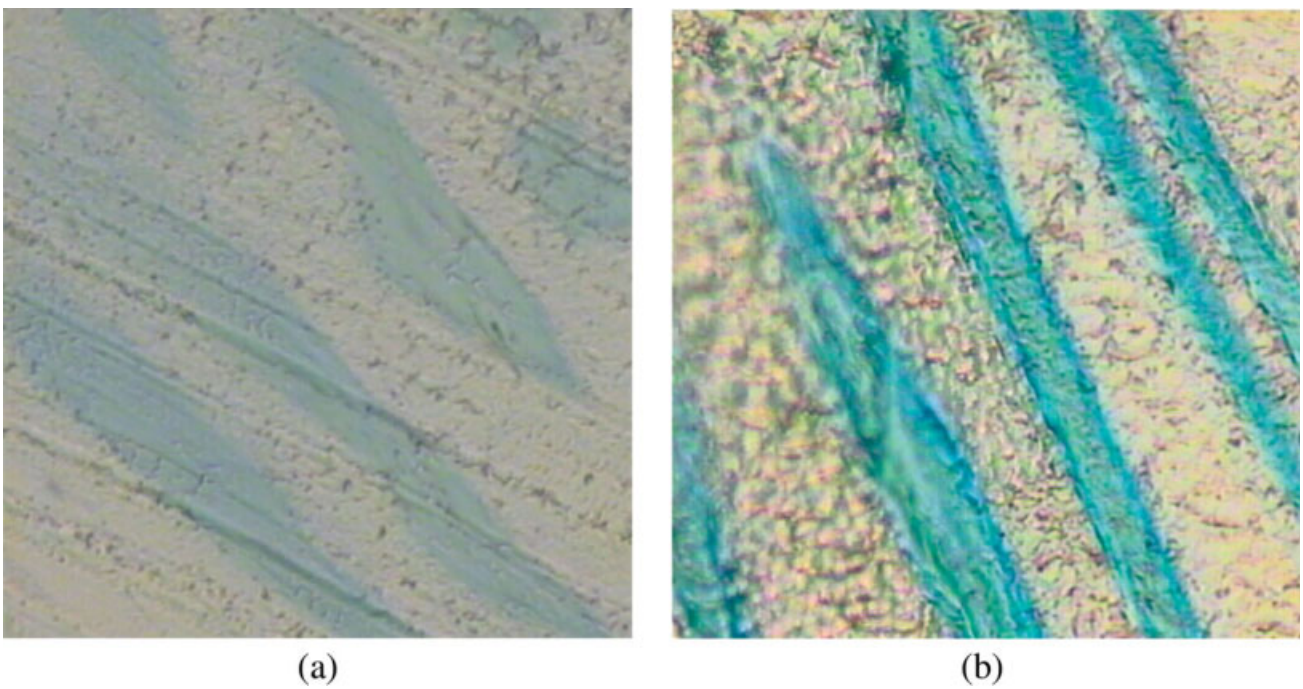

Figure 12 **(a)** Longitudinal section of untreated dyed CA fabric. Dyeing: 1% (o.w.f.) C.I. Disperse Red 82, 80°C, 1 h, pH 5.5, liq. ratio 1 : 50. (b) Longitudinal section of pretreated dyed CA fabric. Treatment: padding, pick up 100%, 0.2 g CD/100 g fiber, pH 8.0, 150°C, 3 min. Dyeing: 1% (o.w.f.) C.I. Disperse Red 82, 80°C,1 h, pH 5.5, liq. ratio 1 : 50.

followed by thermofixation at 150°C for 3 min are depicted in Figure 10(a,b). Some changes on the surface features of the pretreated CA were observed. The cross- and longitudinal sections of the untreated and pretreated CA dyed with C. I. Disperse Red 82 at 80°C for 1 h are shown in Figures 11(a,b) and 12(a,b). It can be noticed that the depth of the dye in the interior structure of the fiber increased as a result of CD treatment followed by thermofixation (Table II). The mean depth of the disperse dye inside the pretreated CA fiber was found to be twice more than that of the dyed untreated one.

From the cross- and longitudinal sections [Figs. 11(a)–12(b)], the % mean depth of dye into the dyed fiber is ranged from 60 to74% for CD-treated CA [Figs. 11(b) and 12(b)] when compared with 20–21% for untreated one [Figs. 11(a) and 12(a)]. It was reported elsewhere that a mean dye depth <30% inside the fiber is defined as ring dyeing.[23,24]

Fastness properties

Both washing and crocking fastness for the dyed untreated and pretreated CA fabrics with C. I. Disperse Red 82 at 80°C for 1 h were carried out. A mean value of 3–4 was determined for the untreated one when compared with 4–5 for the pretreated CA. The presence of CD may exhibit a protective effect for the dyed CD-treated CA fabric toward washing and crocking tests. This resulted in some improvement in the fastness properties.

CONCLUSIONS

This study was concerned with the ability to improve the dyeability of CA fabric with disperse dye by the pretreatment with CD. The treatment conditions were thoroughly investigated. CD treatment was found to improve the color intensity of CA fabric as well as the fastness properties. Also, dyeing of CA fabric at low temperature was achieved. CD treatment may overcome the ring dyeing phenomenon as it increased the depth of dye inside the fiber structure to about 70%, while keeping the thermal stability of CA fabric unchanged.

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