Technological Evaluation of Reactive Cyclodextrin in Cotton Printing with Reactive and Natural Dyes

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ABSTRACT: The chemical modification of cotton fabric with reactive cyclodextrin (R-CD) at different concentrations was carried out to enhance the printability of cotton fabric. The extent of the modification reaction was expressed as %N. Reactive and natural dyes were used to print cotton fabric before and after modification. Printing pastes were applied immediately after preparation or after 24 h of storage. Printing fixation was performed through either steaming or thermal treatment. The effect of the incorporation of R-CD in the printing paste of unmodified cotton was also studied. The results reveal that the extent of the modification reaction increased with increasing R-CD concentration and so did the color strength (K/S) of the printed sample regardless of the dye used. The results also revealed that K/S of the R-CD modified cottons were higher than that of the corresponding unmodified samples regardless of the method of fixation or the time elapsed before printing. On the other hand, the incorporation of R-CD in the printing pastes of reactive dyes, namely, Cibacron Brown 6R-P or Remazol Brilliant Red GG, had adverse effects, most probability due to the (a) increasing viscosity of the paste and/or (b) interaction of the reactive dye with R-CD hydroxyls. The opposite held true when a natural dye was used. Further, the incorporation of R-CD in the printing pastes had no effect on the rheological type of the pastes or the on overall fastness properties of the prints. Nevertheless, such an incorporation of R-CD was accompanied by a remarkable increase in the magnitude of the apparent viscosity. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 338–347, 2006

Key words: dyes/pigments; modification; viscosity

INTRODUCTION

Cotton is the most widely used natural textile fiber in the world. Its preeminence is due to a happy combination of properties such as abundance; a reasonable, fine cross-section; high strength and durability; the ability to absorb moisture; and easy dyeability. However, cotton has some drawbacks, including little resistance to bacteria, fungi, heat, and weathering effects; low wrinkle resistance; and the inability to maintain shape and creases, especially in moist weather. To overcome one or more of such drawbacks, a great deal of research and technical work has been directed toward the preparation of modified cottons with many useful and novel properties and the retention of its valuable fibrous nature.[1] These studies have included partially carboxymethylated cotton,[2–4] acetylated cotton,[5] cyanoethylated cotton,[6] carbamoylethylated cotton,[7] acrylamidomethylated cotton, and the carbamate of cotton cellulose.[8] In recent years, cyclodextrins have represented an important group of auxiliaries in textile finishing[9,10] because of the growing requirement for biodegradability in the auxiliaries used.[11] The monochlorotriazinyl derivative of β-cyclodextrin is one such auxiliaries that is commercially available.[12]

This study was undertaken to chemically modify cotton fabric with a reactive cyclodextrin (R-CD), namely, the monochlorotriazinyl derivative of β-cyclodextrin, and to study the printability of the obtained modified cotton with either reactive or natural dyes. The incorporation of the R-CD in the printing pastes of these dyes and the onset of this on the color strength (K/S) and overall fastness of the prints were also studied. Furthermore, the rheological properties of the printing pastes were examined.

EXPERIMENTAL

Materials

Cotton fabric

Cotton poplin fabric (140 g/m^2) supplied by Misr/Helwan for Spinning and Weaving Co. (Cairo, Egypt) was used throughout this study.

Thickening agents

Dial gin LV 100, a low-viscosity sodium alginate, was kindly supplied by BF Godlich Diamalt GmbH (Mu-

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nichen, Germany). Ciba Alco print DICS synthetic thickener was an acrylic polymer dispersion and was compatible with all anionic and nonanionic auxiliaries that are normally used in printing. This synthetic thickener was kindly supplied by Ciba Specialty Chemicals (Cairo, Egypt).

Reactive dyes

Cibacron Brown 6R-P was kindly supplied by Ciba-Geigy (Switzerland); its reactive center was monochlorotriazine. Remazol Brilliant Red GG was kindly supplied by Dyestar; its reactive center was vinyl sulfone.

Natural dye

Lawsonia Intermis Linn lythracease (henna) was used without further purification. It was purchased from a local market in Egypt in a powder form.

Binder

Printofix Binder MTB was kindly supplied by Clarient.

Other chemicals

Monochlorotriazinyl-β-cyclodextrin (R-CD) was kindly supplied by Wacker-Chemie GmbH (Munchen, Germany). Sodium carbonate, sodium bicarbonate, ferrous chloride, and urea were laboratory-grade chemicals. A mild oxidizing agent (Medoxy T) was kindly supplied by Dr. Ibrahim Hassan's Co.

Methods

Reaction of cotton fabric with R-CD

The conventional pad–dry–thermofixation method was applied. The pad bath containing R-CD and the catalyst (sodium hydrogen carbonate) was prepared as follows. A small amount of water was added to R-CD, and the resulting solution was warmed until complete dissolution occurred. The solution was then cooled to room temperature, and the pad-bath concentration was adjusted with concurrent addition of the catalyst (20 g/L sodium bicarbonate). Cotton fabric was padded in the bath twice to a wet pickup of 100%. The treated fabric was dried in an oven for 13 min at 60–70°C and was then subjected to heat treatment at 150°C for 7 min. Different concentrations of R-CD (50, 75, and 100 g/L) were used to obtain different extents of reaction.

Printing

Preparation of the printing pastes. The printing pastes of the reactive dyes were prepared with the following recipe: 40 g of reactive dye, 100 g of urea, a variable amount of sodium alginate thickener (50 g/kg of printing paste), 30 g of sodium bicarbonate, 10 g of resist salt, and a variable amount of water, for a total recipe of 1000 g.

Use of printing paste with a r-cd. The incorporation of R-CD at different concentrations in the printing paste was studied. Thus, different printing pastes were prepared according to the aforementioned reactive printing pastes along with the following additives: R-CD at 50, 75, or 100 g/kg of printing paste.

Printing pastes for the application of henna. The pastes used for the application of henna powder as a pigment color in printing were prepared as follows: 100 g of henna, a variable amount of Ciba Alco print synthetic thickener (25 g/kg), 100 g of Printofix MTB binder, 12.5 g of diammonium phosphate, 40 g of urea, and a variable amount of water, for a total recipe of 1000 g.

The binder was added to the thickening agent, and the whole stock was mixed well. The henna powder was then added to the stock thickening followed by the addition of the acid catalyst. Finally, water was added to complete the weight of the printing paste to 1 kg.

Effect of the addition of R-CD. The R-CD was added to the henna printing paste. Different printing pastes were prepared containing henna, synthetic thickener, binder, and urea along with different concentrations of R-CD at 50, 75, or 100 g/kg of the printing paste.

Printing technique. A screen printing technique was applied to the modified and unmodified cotton fabrics.

Fixation. The fixation of the printed goods was done by either steaming or thermal treatment through the use of an automatic thermostatic oven (Wenner Mathis Co., Switzerland). Steaming was conducted at 100–103°C for 15 min for reactive dyes or at 125°C for 25 min for the henna dye. On the other hand, thermofixation time and temperature were adjusted according to the dye as follows:

- Goods printed with Cibacron Brown 6R-P were fixed at 150°C for 3.5 min.
- Goods printed with Remazol Brilliant Red GG were fixed at 145°C for 4 min.
- Goods printed with henna were fixed at 160°C for 4 min.

Washing. The washing of the printed goods with reactive dyes was carried out through five stages as follows:

- Thorough rinsing with cold water.

- Treatment with hot water.
- Treatment near the boiling temperature (90–95°C) with a solution containing 5 g/L Hostapal CV and 2 g/L sodium carbonate.
- Washing with hot water.
- Rinsing with cold water.
- Last, drying and assessment for K/S and overall fastness properties.

Washing of the printed goods with henna was carried out as follows:

- The printed goods were rinsed thoroughly with cold water.
- They were then soaped for 15 min at 45°C in a solution containing 5 g/L Hostapal CV and 2 g/L sodium carbonate and then washed with hot water.
- Finally, the goods were washed with cold water, air-dried, and assessed for K/S and overall colorfastness properties.

Analysis and testing

Determination of the nitrogen content

Nitrogen content was determined by the Cole and Parks modification of the semimicro Kjeldahl method.[13]

Determination of the rheological properties[14]

The rheological properties of the printing pastes were measured with a Rheomat-15 at 25°C, and the apparent viscosity (η) at various rates of shear (D's) was calculated from the shearing stress and D as follows:

$$\eta = \frac{\tau}{D}$$

Color measurements[15,16]

K/S and the overall fastness properties (washing, perspiration, and crocking) were assessed according to the standard methods.

RESULTS AND DISCUSSION

R-CD: tentative mechanism

Monochlorotriazinyl-β-cyclodextrin is represented in the following structure:[17]

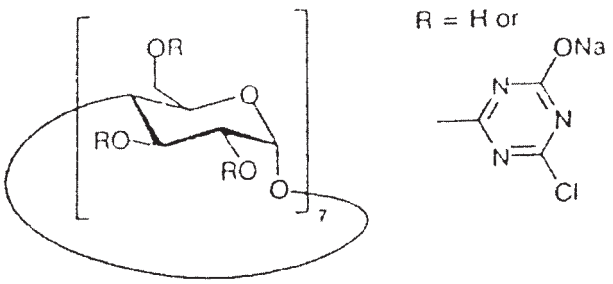

TABLE I
Dependence of the Extent of the Reaction (%N) of R-CD with Cotton Cellulose on R-CD Concentration

R-CD concentration (g/L)	%N
50	0.15
75	0.30
100	0.50

Because the degree of substitution ranged from 0.3 to 0.5, we determined that one hydroxyl group in at least every two anhydroglucose units of the cyclodextrin would be substituted by the monochlorotrizinyl moiety. For convenience, the monochlorotriazinyl-β-cyclodextrin is referred to as R-CD, where R and CD are the reactive monochlorotriazinyl and β-cyclodextrin moieties, respectively.

As an electrophilic compound, R-CD reacts in the presence of alkali with nucleophilic groups, such as the hydroxyl groups of cellulose (Cell), as shown in eq. (1):

$$\text{Cell-OH} + \text{R-CD} \xrightarrow{\text{Alkali}} \text{Cell} - \text{O} - \text{CD}$$

The reaction involves covalent binding to the cellulose and, therefore, can be categorized as a reaction that induces the chemical modification of cellulose.

With this in mind, it was of great interest for us to investigate the influence of the presence of the aforementioned R-CD in the molecular structure of cellulose on the behavior of the latter toward printing with either reactive or natural dyes. Hence, samples of the cotton fabrics were allowed to react with different concentrations of R-CD according to the procedure described in the Experimental section. After treatment and fixation, the treated fabrics were thoroughly washed to remove the unfixed R-CD; they were then dried. At this end, the fabric samples were monitored for nitrogen content. The results are given in Table I.

It was clear (see Table I) that the extent of the reaction (%N) between cellulose hydroxyl and R-CD increased from 0.15 to 0.50% when the R-CD concentration was increased from 50 to 100 g/L. This significant increase in %N could be interpreted in terms of a greater availability of R-CD in the proximity of the hydroxyl groups of cotton cellulose. It is understandable that the cellulose hydroxyl groups were immobile, and hence, the reaction of these hydroxyl groups would have relied on the availability of R-CD molecules in their vicinity, a point that was justified at higher R-CD concentrations.

The printability of R-CD modified cotton fabric samples toward reactive and/or natural dyes are given next.

TABLE II
Printability of R-CD Modified Cottons Having Different Nitrogen Contents when Printing Was Performed with Either Cibacron Brown 6R-P or Remazol Brilliant Red GG

		K/S of fabrics printed and fixed via			
		Steaming		Thermofixation	
Substrate	%N	Freshly prepared	Stored for 24 h	Freshly prepared	Stored for 24 h
Untreated cotton	—	6.93 (1.73)	6.61 (1.73)	6.50 (0.64)	6.28 (0.26)
I	0.147	7.80 (2.26)	7.65 (2.69)	6.73 (0.86)	6.60 (0.63)
II	0.299	7.96 (2.52)	7.65 (2.83)	6.84 (0.89)	6.61 (0.67)
III	0.497	8.29 (2.67)	8.12 (2.88)	7.10 (0.99)	6.97 (0.80)

The values in parentheses represent the results obtained when Remazol Brilliant Red GG was used. **I** = cotton prepared with 5% R-CD; **II** = cotton prepared with 7.5% R-CD; **III** = cotton prepared with 10% R-CD.

Printing with a reactive dye that reacted by substitution

The R-CD modified cotton and the unmodified cotton were printed with a monochlorotriazine reactive dye, namely, Cibacron Brown 6R-P. The fixation of the dye was effected through steaming or thermofixation before and after storage for 24 h. The printed samples were monitored for K/S, and the results obtained are given in Table II.

It was clear (see Table II) that the K/S of the R-CD modified cotton fabric samples was relatively higher than that of the untreated cotton sample regardless of the method of fixation and/or the time elapsed before printing. It was also clear that as the %N increased, the K/S of the printed fabric increased. The increase in K/S by modification of cotton with R-CD may have been due to one or more of the following reasons: (1) the increase in the number of free hydroxyl groups present in R-CD itself, (2) the inclusion of the dye molecules in the cone-shaped cyclodextrin molecules, or (3) the physicochemical changes of the R-CD modified cotton fabrics.

TABLE IV
Effect of the Addition of Different Amounts of R-CD to the Printing Pastes of Either Cibacron Brown 6R-P or Remazol Brilliant Red GG on the K/S of the Printed Samples

	K/S of the fabrics printed and fixed via			
	Steaming		Thermofixation	
Amount of R-CD (g/kg) printing paste	Freshly prepared	Stored	Freshly prepared	Stored
None	6.93 (1.73)	6.61 (1.73)	6.50 (0.64)	6.28 (0.26)
50	6.24 (1.54)	6.39 (1.78)	6.73 (0.30)	5.98 (0.26)
75	6.08 (1.48)	5.89 (1.73)	5.79 (0.18)	5.62 (0.16)
100	5.79 (1.19)	5.45 (1.23)	4.73 (0.12)	5.37 (0.12)

The values in parentheses represent the results obtained when Remazol Brilliant Red GG was used.

Table III reveals that the colorfastness properties for rubbing, washing, and perspiration of R-CD modified cotton fabric samples were very comparable with those obtained for the unmodified cotton sample. This implied that the presence of cyclodextrin moieties in the molecular structure of the printed cotton cellulose did not detract from its overall fastness properties.

The effect of the addition of R-CD at concentrations of 50, 75, and 100 g/kg to the printing paste containing Cibacron Brown 6R-P on K/S and the overall fastness properties of the printed goods are shown in Tables IV and V, respectively.

TABLE III
Fastness Properties of Cotton Fabrics Chemically Modified with R-CD and Printed with Either Cibacron Brown 6R-P or Remazol Brilliant Red GG (Freshly Prepared)

					Perspiration fastness			
	Washing fastness at 90°C		Rubbing fastness		Acidic		Alkaline	
Substrate	Staining	Alteration	Dry	Wet	Staining	Alteration	Staining	Alteration
Untreated	4 (4–5)	4 (4–5)	3 (3–4)	3 (3–4)	3–4 (4)	4 (4)	4 (4)	4–5 (4–5)
I	4 (4)	4 (4)	3 (4)	3 (4)	2–3 (4)	3 (4–5)	2–3 (4)	4 (4–5)
II	4–5 (4–5)	4–5 (4–5)	3 (4)	3 (4)	3 (4)	4 (4–5)	3 (4)	4 (4–5)
III	4–5 (4–5)	4–5 (4–5)	3 (3–4)	3 (3–4)	3 (4)	3–4 (4)	3 (4)	4 (4–5)

The values in parentheses represent the results obtained when Remazol Brilliant Red GG was used. Fixation was carried out via steaming. **I** = cotton prepared with 5% R-CD; **II** = cotton prepared with 7.5% R-CD; **III** = cotton prepared with 10% R-CD.

TABLE V
Effect of the Addition of Different Amounts of R-CD on the Colorfastness Properties of the Printed Samples with Freshly Prepared Pastes Containing Either Cibacron Brown 6R-P or Remazol Brilliant Red GG

Amount of R-CD (g/kg) printing paste	Washing fastness at 90°C		Rubbing fastness		Perspiration fastness			
					Acidic		Alkaline	
	Staining	Alteration	Dry	Wet	Staining	Alteration	Staining	Alteration
None	4 (4–5)	4 (4–5)	3 (3–4)	3 (3–4)	3–4 (4)	4 (4)	4 (4)	4–5 (4–5)
50	4 (4–5)	4 (4–5)	3–4 (4)	3–4 (4)	2–3 (4)	3–4 (4)	3 (4)	4 (4–5)
75	4 (4–5)	4 (4–5)	3–4 (4)	3–4 (4)	3 (4)	3 (4–5)	3–4 (4)	4 (4–5)
100	4–5 (4–5)	4–5 (4–5)	4 (4)	3–4 (4)	3 (4)	3 (4–5)	3–4 (4)	4–5 (4–5)

The values in parenthes represent the results obtained when Remazol Brilliant Red GG was used. Fixation was carried out via steaming

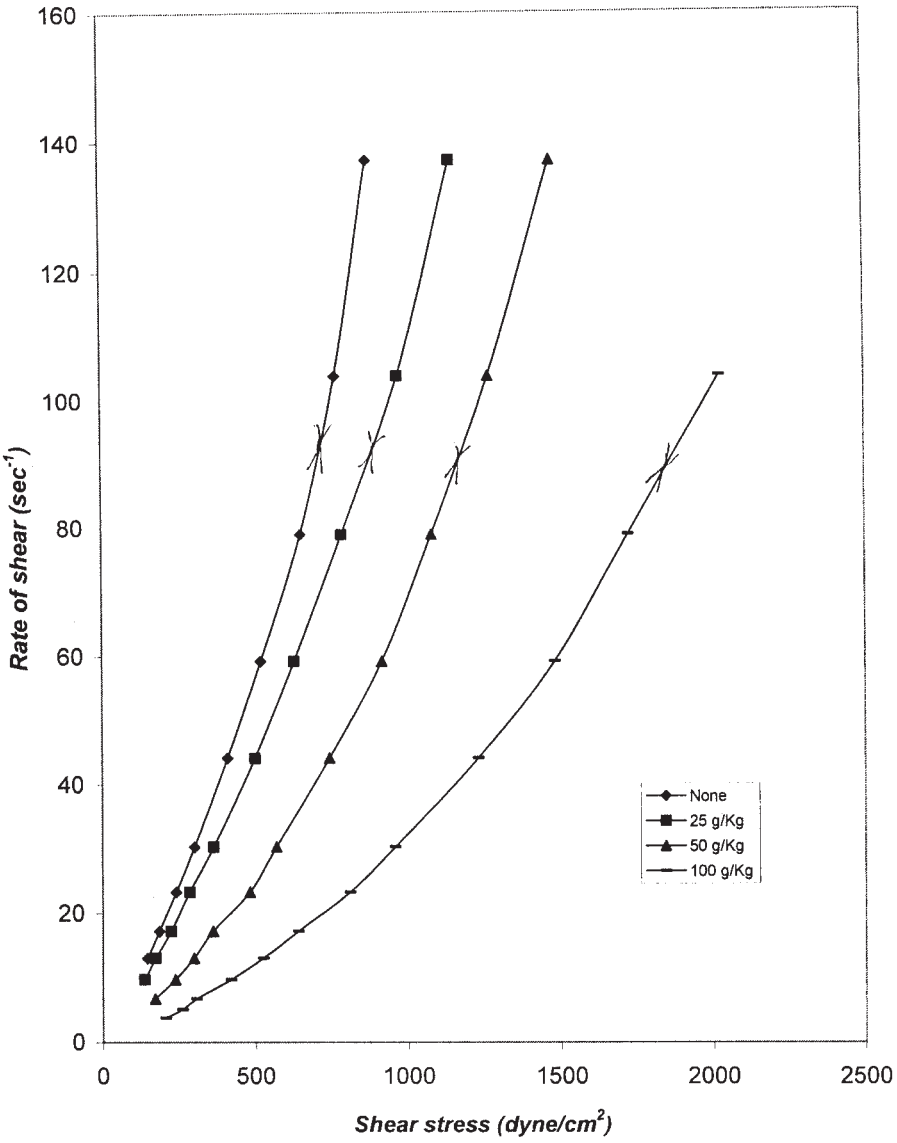

Figure 1 Influence of the addition of R-CD to the printing pastes of Cibacron Brown 6R-P on the rheological properties of the pastes before storage.

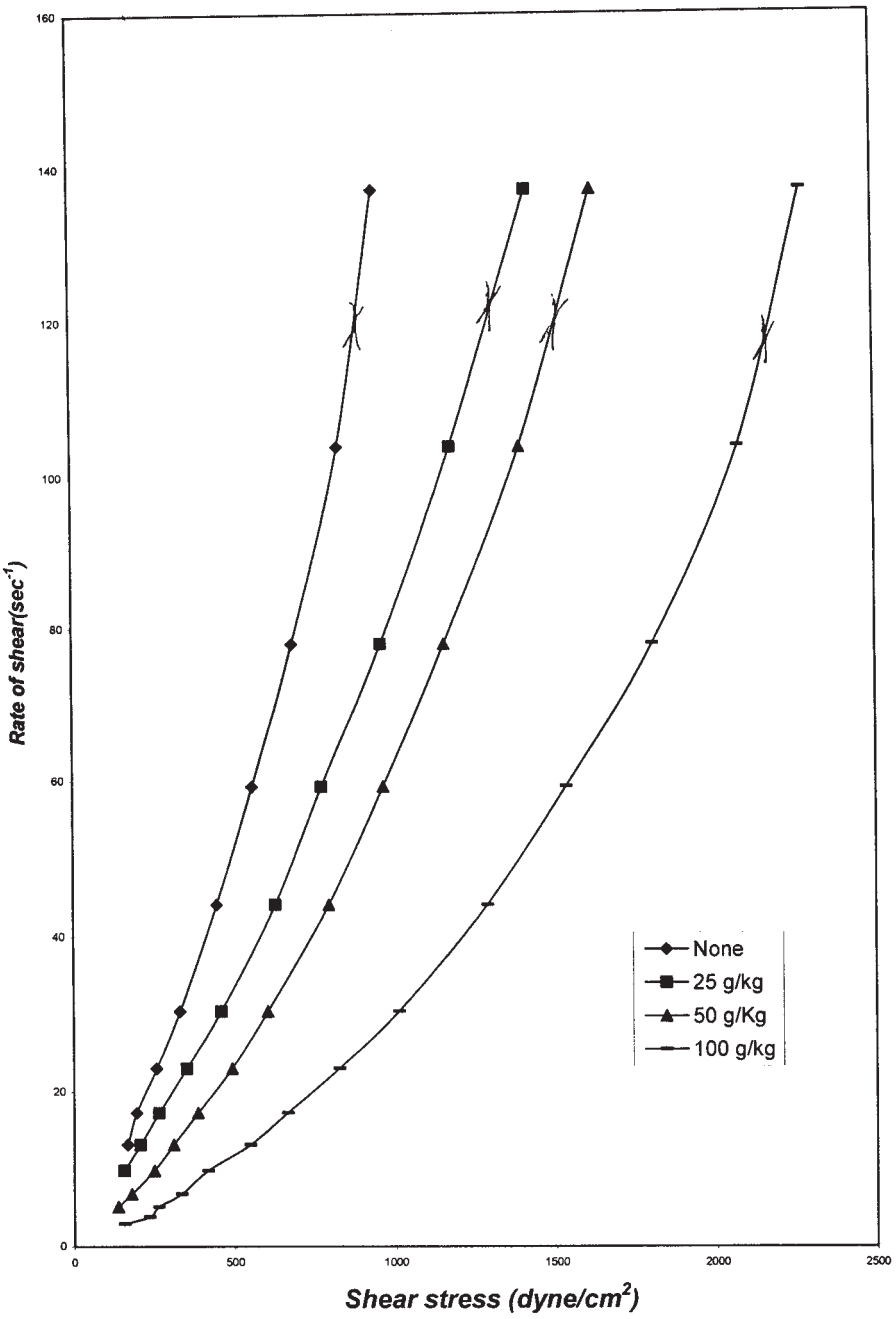

Figure 2 Influence of the addition of R-CD to the printing pastes of Cibacron Brown 6R-P on the rheological properties of the pastes after 24 h of storage.

Table IV shows that incorporation of R-CD in the printing paste had an adverse effect because, in all cases, the K/S values obtained in the presence of R-CD was less than those values obtained when the sample was printed with the conventional printing paste without R-CD.

Table IV also shows that for cotton samples printed with pastes containing R-CD and fixed either by steaming or thermofixation, K/S decreased as the amount of R-CD in the printing paste increased. This adverse effect of the presence of R-CD in the reactive dye printing paste was more pronounced with the Remazol dye, which reacted by addition and as shown later.

The decrease in K/S brought about by the incorporation of R-CD in the printing paste of the reactive dye could be associated with the involvement of R-CD with both the printing paste and the dye. It is possible that R-CD increased the viscosity of the printing paste and, in so doing, impeded the diffusion and transfer of the dye from the printing paste to the fiber (fabric) phase. It is also possible that R-CD underwent a reac-

TABLE VI
Effect of the Addition of Different Amounts of R-CD to the Printing Paste of Cibacron Brown 6R-P on η of the Paste at Various D Values Before and After Storage for 24 h

	η (poise) of the printing paste containing R-CD							
	None		50 g/kg		75 g/kg		100 g/kg	
D (s^{-1})	Freshly prepared	Stored	Freshly prepared	Stored	Freshly prepared	Stored	Freshly prepared	Stored
3.851	—	—	—	—	—	—	53.32	53.27
5.139	—	—	—	—	—	26.63	50.61	51.18
6.779	—	—	—	—	25.21	26.34	45.23	49.12
9.771	—	—	14.01	15.86	24.23	25.45	42.87	42.65
13.12	11.10	12.69	13.16	15.69	22.74	23.58	40.06	41.74
17.26	10.70	11.27	12.93	15.32	20.93	22.36	37.12	38.55
23.03	10.43	11.18	12.36	15.25	20.92	21.39	35.19	35.90
30.38	9.91	10.91	11.98	15.13	18.74	19.91	31.54	33.35
44.10	9.31	10.12	11.36	14.27	16.88	18.06	27.93	29.24
59.22	8.79	9.43	10.63	13.08	15.48	16.32	25.05	25.93
77.92	8.09	8.78	9.90	12.33	13.87	14.86	22.13	23.19
103.9	7.38	7.98	9.36	11.35	12.2	13.43	19.50	19.98
137.1	6.39	6.90	8.38	10.38	10.28	11.85	—	16.61

tion with the dye. The ultimate effect of these two possibilities would have certainly led to a decreased K/S. That is, the decrease in K/S was a manifestation of the interactions of the R-CD with the printing paste and the reactive dye.

Influence of the addition of R-CD to the printing paste on the rheological properties. Figures 1 and 2 show the influence of the addition of R-CD at concentrations of 50, 75, and 100 g/kg to the printing paste of Cibacron Brown 6R-P on the rheological characteristics of the printing paste before and after storage for 24 h, respectively. As was evident, the presence of R-CD in the printing paste had no influence on the rheological type of the pastes; the pastes displayed non-Newtonian pseudoplastic behavior before and after the addition of R-CD (Fig. 1). Nevertheless, presence of R-CD had a remarkable effect on the magnitude of η, as discussed later.

Figure 2 depicts that storage of the printing pastes under investigation for 24 h before the rheological measurements were performed did not produce any significant effect on the rheological type of the pastes. The latter samples exhibited pseudoplastic behavior. On the other hand, storage did affect η, as shown.

Table VI discloses that an increase in the amount of R-CD from 0 to 100 g/kg of printing paste was accompanied by a substantial increase in η from 11.10 to 40.06 poise, respectively, at a D of 13.12 s^{-1}. The storage of the pastes for 24 h also caused an increase in η at the same D.

The increase in η with increasing R-CD suggests that the R-CD provided extra viscosity to the paste, particularly via swelling, and thereby produced a mechanical hindrance to the flow of the paste. Nevertheless, the formation of large molecules through the interactions of R-CD with both the thickener and the dye and their positive impact on η could not be ruled out.

TABLE VII
Influence of the Extent of the Reaction (%N) of R-CD with Cotton Cellulose on its Printability with a Natural Dye (Henna)

		K/S of fabrics printed and fixed via			
		Steaming		Thermofixation	
Substrate	%N	Freshly prepared	Stored	Freshly prepared	Stored
Untreated cotton	—	0.89	1.34	0.23	0.36
I	0.147	1.14	1.60	0.65	0.40
II	0.299	1.27	1.64	0.96	0.43
III	0.497	1.30	1.65	1.05	0.45

I = cotton prepared with 5% R-CD; **II** = cotton prepared with 7.5% R-CD; **III** = cotton prepared with 10% R-CD.

Printing with a reactive dye that reacted via addition

The printability of the modified cotton in question with a reactive dye that reacted via addition, namely, Remazol Brilliant Red GG, was investigated. Three R-CD modified cotton samples with different nitrogen contents along with the untreated cotton were printed with printing pastes containing the said Remazol dye. The printing paste was used both immediately after preparation and after being stored for 24 h. After printing, the samples were fixed via either steaming or thermofixation, washed, dried, and assessed for K/S and overall fastness properties. The results obtained are summarized in Tables II and III.

As shown in Table II, the K/S values of the R-CD modified cotton fabrics were considerably higher than

TABLE VIII
Fastness Properties of R-CD Modified Cotton Fabrics Printed with a Natural Dye (Henna)

	Washing fastness at 50°C		Rubbing fastness		Perspiration fastness			
					Acidic		Alkaline	
Substrate	Steaming	Alteration	Dry	Wet	Steaming	Alteration	Steaming	Alteration
Untreated	4–5	4–5	4	4	4–5	4–5	4–5	4–5
I	4–5	4–5	4	4	4–5	4–5	4	4–5
II	4–5	4–5	3–4	3–4	4–5	4–5	4–5	4–5
III	4–5	4–5	4	4	4	4–5	4	4–5

Fixation was carried out via steaming. **I** = cotton prepared with 5% R-CD; **II** = cotton prepared with 7.5% R-CD; **III** = cotton prepared with 10% RCD.

those of the untreated cotton fabric. However, the magnitude of K/S relied on (1) the extent of modification (expressed as %N), (2) the method of fixation, and (c) the time elapsed before printing. Thus, the K/S for R-CD modified cotton samples that were printed and fixed by steaming was higher than that of those fixed by thermofixation. Furthermore, regardless of the method of fixation and/or the storage time, K/S increased with increasing %N of the chemically modified cotton. For example, samples printed with freshly prepared paste and fixed by steaming acquired K/S values that increased from 1.73 to 2.67 by increasing the %N from 0 to 0.50, respectively. This finding was in conformation with that found with Cibacron Brown 6R-P and could be similarly explained.

The surprising feature in the results of Table II is that the storage of the printing paste caused a slight increase in the K/S of the chemically modified cotton printed and fixed by steaming; meanwhile, it caused a serious decrease in the K/S of samples printed and fixed by thermofixation. The manufacturer of Remazol Brilliant Red GG recommended fixation of this dye by thermal means was not advisable.

The positive effect of storage on the K/S of samples fixed by steaming suggests that the storage of the pastes for 24 h did not cause dye hydrolysis; at the same time, storage acted in favor of the compatibility and homogeneity of the printing paste.

TABLE IX
Effect of the Addition of Different Amounts of R-CD to the Printing Pastes of Henna on the K/S of the Printed Samples

	K/S of the fabric printed and fixed via			
	Steaming		Thermofixation	
Amount of R-CD (k/kg)	Freshly prepared	Stored	Freshly prepared	Stored
None	0.89	1.34	0.23	0.36
50	0.91	1.35	0.23	0.42
75	0.93	1.39	0.48	0.50
100	1.03	1.40	0.49	0.54

Table III shows the overall colorfastness properties of R-CD modified cotton, along with those of the unmodified sample. It is clear that the modification of cotton through the reaction with R-CD improved the K/S of the prints without impairing the colorfastness to washing, rubbing, or perspiration.

Table IV shows the results of K/S obtained when different amounts of R-CD (50, 75, and 100 g/kg of paste) were incorporated in the printing paste containing Remazol Brilliant Red GG.

In conformation with the results obtained with the Cibacron Brown 6R-P dye, the addition of R-CD to the printing paste containing Remazol Brilliant Red GG caused a remarkable decrease in the K/S of the printed fabric. This was the case regardless of (1) the amount of R-CD in the paste, (2) the method of fixation, and (3) the time of storage. An interpretation of this data could be made on the basis of lines drawn previously for the Cibacron Brown 6R-P dye.

Table V illustrates the overall fastness properties of the unmodified cotton fabric samples printed with printing pastes containing different amounts of R-CD. As is evident, the presence of R-CD in the printing paste had no remarkable effect on the overall fastness properties because it was easily washable, as previously indicated.

Printing with a natural dye

The aim of this section of the study was to investigate the effect of presence of R-CD either chemically bonded with cotton cellulose or as additives in the printing paste on the printability of cotton with a natural dye, namely, henna. To achieve this goal, a printing paste containing henna was prepared according to the recipe mentioned in the Experimental section.

Chemically modified cottons with R-CD containing different nitrogen contents (0.15, 0.30, and 0.50) were printed with henna paste. Furthermore, printing pastes containing different amounts of R-CD (50, 75, and 100 g/kg of printing paste) were also prepared

TABLE X
Effect of the Addition of Different Amounts of R-CD on the Colorfastness Properties of the Printed Samples with Freshly Prepared Pastes Containing Henna

Amount of R-CD (g/kg) printing paste	Washing fastness at 50°C		Rubbing fastness		Perspiration fastness			
					Acidic		Alkaline	
	Staining	Alteration	Dry	Wet	Staining	Alteration	Staining	Alteration
None	4–5	4–5	4	4	4–5	4–5	4–5	4–5
50	4–5	4–5	4	4	4–5	4–5	4	4–5
75	4–5	4–5	4	4	4	4–5	4	4–5
100	4–5	4–5	4	4	4–5	4–5	4–5	4–5

Fixation was carried out via steaming.

and used in the printing samples of untreated cotton. After printing, drying, fixation, washing, and drying, the printed samples were assessed for K/S and overall fastness properties. The results obtained are given in Tables VII–X.

Table VII shows the values of K/S for R-CD modified cotton samples before and after storage for 24 h. By and large, K/S depended on (1) the degree of modification (expressed as %N), (2) the type of fixation, and (3) storage of the paste before printing. The K/S values of the R-CD modified cotton triazinyl cyclodextrin samples were higher with higher nitrogen contents. These K/S values were also higher than their corresponding values for the untreated cotton samples. This indicated that the presence of triazinyl cyclodextrin in the molecular structure of the cotton enhanced its printability with the henna natural dye.

The increase in the K/S of the R-CD chemically modified cotton may have been due to the presence of the cyclodextrin moiety, which included the small molecule of lawsone (2-hydroxy-l,4-naphthoquinone, the colored material in henna), which fit into its cone-shaped hydrophobic cavity.[18,19] Hence, we expected that as the amount of combined R-CD on cotton increased, the K/S increased as well.

It is also clear from the data shown in Table VII that the K/S values of the samples printed and fixed by steaming were higher than their corresponding samples printed and fixed by thermofixation. Also, storage caused an increase in K/S for samples fixed by steaming and a decrease in K/S for samples fixed by thermofixation.

This finding may be interpreted in terms of the increased dissolution of henna molecules in the condensed water and their migration to the surface in case of steaming. It is understandable that moisture was higher and the time was longer in the case of fixation by steaming than that of fixing by thermofixation.

Table VIII shows that the presence of R-CD in the molecular structure of cotton cellulose had no effect on the colorfastness properties to washing, rubbing, or perspiration.

Table IX shows the K/S values for untreated cotton printed with henna paste containing different amounts of R-CD (0, 50, 75, and 100 g/kg of printing paste). It was obvious that the incorporation of R-CD in the printing paste was accompanied by an increase in K/S. This was observed regardless of the method of fixation and the storage time, with the same differences caused by these two parameters shown previously with the reactive dyes. Also, K/S values obtained on the incorporation of the R-CD in the printing paste were much lower than those obtained with the R-CD modified cotton.

Table X shows the colorfastness properties, namely, to washing, rubbing, and perspiration, for the untreated cotton fabrics printed with henna pastes containing different amounts of R-CD. The results make it evident that there was no remarkable difference between these samples and the sample printed with paste free from R-CD.

CONCLUSIONS

Samples of cotton fabric were chemically modified with R-CD. This was done to enhance the printability of the fabric. The results obtained led to the following conclusions:

- The extent of reaction (expressed as %N) increased with increasing concentration of R-CD.
- With either reactive or natural dyes, the K/S of R-CD modified cotton was higher than that of the untreated samples regardless of the method of fixation or the storage time of the paste, and the K/S increased with increasing %N of the fabric.
- The overall fastness properties of R-CD modified cotton fabrics were very comparable with those of the unmodified cotton samples.
- Incorporation of R-CD in the printing pastes of Cibacron Brown 6R-P or Remazol Brilliant Red 6R-P had an adverse effect on the K/S of the printed samples due to (1) an increase in the viscosity of the paste and/or (2) the interaction of the reactive dye with R-CD hydroxyls. The opposite held true when the henna natural dye was used.

- Incorporation of R-CD in the printing pastes had no effect on the rheological type of the pastes or the overall fastness properties of the prints. Nevertheless, such an incorporation of R-CD was accompanied by a remarkable increase in the magnitude of η values of the pastes.

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