Permanent Fixation of β-Cyclodextrin on Cotton Surface—An Assessment Between Innovative and Established Approaches

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ABSTRACT: Attachment of β-cyclodextrin (β-CD) molecules on cotton textile provides hosting cavities that can include a large variety of guest molecules for specific functionality. Five different new and existing techniques were evaluated for connecting β-CD and its derivatives to cotton surface. A comparison has been made in terms of maximum attachment of β-CD on cotton surface. Novel chemical based crosslinking with homo-bi-functional reactive dye (C.I. reactive black 5) and grafting with reactive monochlorotriazinyl-β-cyclodextrin show maximum attachment to cotton surface. Innovative, enzymatic coupling of especially synthesized 6-monodeoxy-6-mono(*N*-tyrosinyl)-β-cyclodextrin was performed on cotton textile surface. Enzymatic coupling was also carried out in a homogeneous system and attachment confirmed by UV–vis spectroscopy. This tyrosinase mediated coupling is low temperature and very specific technique. A phenolphthalein based analytical method was partially modified to reliably measure the amount of attached β-CD on cotton surface. Atomic force microscopy and scanning electron microscopy techniques were used for surface characterization of the treated and untreated cotton surfaces. Alteration in surface topography has been observed for β-CD treated samples. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4090–4097, 2012

Key words: β-Cyclodextrin; chemical grafting; enzymatic coupling; tyrosinase; functional cotton textiles

INTRODUCTION

Cotton based textile materials are versatile and widely used. Properties and functionalities of such materials are affected by physical–chemical treatments at micro, nano, meso, and macroscopic levels. The open permeable structure and large surface area makes textile materials a useful basis to bring new functionalities.[1] Owing to the enormous progress over the years in supramolecular chemistry, nanobiotechnology, and polymer technology, high performance functionalized textiles have been developed.[2–8] This manuscript will essentially focus on aspects of functional textile bearing cyclodextrins.

β-Cyclodextrin (β-CD) has been selected as host system because of their ability to form inclusion complexes with a variety of long-chain aliphatic or aromatic molecules. β-CD is from a toxicological point of view considered to be safe and licensed as food additives. β-CD and its several derivatives are commercially available in large quantities.[4] A variety of chemical and physical techniques exist for the production of textile fibers bearing cyclodextrins at their surfaces. Cyclodextrins can be fixed to the surface of textile fibers permanently or nonpermanently. Permanent fixation can be achieved via covalent bonding or crosslinking. Selection of best suited attachment technique depends on the end application and type of substrate such as natural or synthetic fibers.[9]

Diverse approaches are described in scientific literature for attaching β-CD to cotton surfaces.[3,6,7,10–12] The cellulose-cyclodextrin copolymer has been described first time in early 90s.[11] Alkali-swollen cellulose fibers were reacted with cyclodextrin and epichlorohydrin. The chemically bound cyclodextrin retained its complex forming ability.[7,11] Another example is grafting procedure with acryl-amidomethylated-β-cyclodextrin (CD-NMA). In this technique cellulose is oxidized by cerium (IV), producing a free radical on the cellulose backbone.[3] Grafting of β-CD on cotton fiber surfaces using chemical linker such as 1,2,3,4,-butane-tetra-carboxylic acid (BTCA) is widely accepted method.[6] A cyclic anhydride is formed, that reacts with hydroxyl groups of cellulose, forming an ester bond under the influence of heat and the presence of a catalyst, such as sodium dihydrogen hypophosphite. Fixation of β-CD

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on cotton surface has also been reported by means of hetero-bi-functional reactive dyes containing monochlorotriazine and vinyl sulfone reactive groups.[12] One of the largely used techniques is grafting with reactive MCT-β-CD that can be covalently linked to nucleophilic substrates, like cellulose, by a condensation reaction.[13,14]

In this article, we will evaluate five different innovative and established attachment techniques of β-CD on cotton surface. Novel β-CD attachment techniques such as crosslinking with homo-bi-functional dye (C.I. reactive black 5/RB5) and tyrosinase mediated enzymatic coupling of Tyr-β-CD are first time evaluated on cotton surfaces. Optimization exercises were conducted and comparison has been made between well established grafting techniques and newly developed coupling techniques in terms of maximum attachment of β-CD on cotton surface.

MATERIALS AND METHODS

Cotton fabric

The substrate used was industrially two sided singed, desized, scoured, bleached, 245 g/m^2 (±5%) plain woven 100% cotton fabric. The fabric sample BD22, was supplied by Ten Cate Technical Fabrics BV, the Netherlands. The uniformity of the fabric sample in terms of pore volume distribution (PVD) was ensured. PVD of the BD22 fabric was measured with an auto-porosimeter[15,16] in receding mode (from low pressure till high pressure) to eliminate the effect of irregular or interconnected pores.

Chemicals

A homo-bi-functional reactive dye, Ramazol Black 5® (C.I. reactive black 5/RB5) was obtained from Sigma with 55% dye content. A hetero-bi-functional reactive dye, Sumifix Supra Blue BRF® (C.I. reactive blue 221/RB221) was obtained from Farbchemie Braun KG, Germany. Cavasol®—a MCT-β-CD was received as gift sample from Wacker-Chemie, Germany and used as received. All other chemicals such as β-CD, Na_2CO_3, NaCl, NaOH, Phenolphthalein (PHP), ethyl alcohol, BTCA, sodium hypophosphite (SHPI) and sodium hydrosulfite ($Na_2S_2O_4$) were analytical grade and purchased from Sigma-Aldrich.

Determination of cyclodextrin contents

The concentration of β-CD and its derivatives grafted to the cotton fabric was determined by the phenolphthalein (PHP) assay method, in which the color fading of an alkaline PHP solution is proportional to the quantity of the cyclodextrin derivative present.[17,18] Method is partially modified for better stability by optimizing proper concentration of PHP and incorporating in Na_2CO_3 solution. This method eliminated variation caused by use of concentrated PHP solution. PHP stock (10 m*M*) was prepared by dissolving 3.1833 mg/mL of ethanol. Several concentrations of β-CD were prepared in 0.05*M* Tris-HCl buffer at pH 7.0. A working PHP solution was made by adding 0.4 mL of 10 m*M* PHP stock, 4.6 mL of ethanol, and 95 mL of 125 m*M* Na_2CO_3 solution just before starting the experiment. Actual calibration was carried out by adding 2 mL of β-CD solution (standards), a circular piece of blank fabric (0.5 g) and 8 mL of working PHP solution giving final PHP concentration of 0.032 m*M*. The test tube was then mixed by vortexing and kept for 15 min. The absorbance was measured at 554 nm on a dual beam UV–vis spectrophotometer (Varian Carry-100®). The cyclodextrin concentration $C_{(\beta\text{-CDfabric})}$ on cotton surface [g/m^2]can be determined as follows;

$$C_{(\beta-\mathrm{CD/fabric})} = M_{\mathrm{CD}}/W_{\mathrm{fabric}} \times \rho_{(\mathrm{fabric})} \quad (1)$$

where M_{CD} is the mass of cyclodextrin in [g], W_{fabric} is the weight of fabric in [g], and density of fabric is 245 g/m^2. The M_{CD} was calculated from the slope of the calibration curve made up of known concentrations of β-CD.

Chemical fixation of β-CD on cotton surface

Four different chemical based β-CD attachment techniques on the fabric samples have been newly developed and adopted. Brief procedures for each type of grafting/crosslinking techniques are given below. All the experiments were performed in duplicate.

Grafting with poly(carboxylic acid) and MCT-β-CD

A procedure for grafting with poly(carboxylic acid) such as BTCA is described earlier.[8] The fabric samples (0.7 g) were immersed in treatment baths for 15 min with different concentrations of β-CD and each 6 g/L of BTCA and SHPI. The predrying of fabric samples were carried out at 110°C for 10 min. The actual fixation was carried out at 200°C for 3 min.[8] Permanent grafting of MCT-β-CD (monochlorotriazinyl-β-cyclodextrin) was carried out according to the procedure already reported in the literature.[10,14] Permanent grafting of MCT-β-CD was carried out by immersing cotton fabric samples for 15 min at room temperature in 125 mm Na_2CO_3 solution. The concentration of MCT-β-CD was varied from 0 to 200 g/L. The squeezed sample then treated at 150°C for 15 min in an oven. Subsequently, samples were washed for 10 min at 60°C to remove any unattached MCT-β-CD. Finally, samples were kept in oven for 1.5 h at 80°C for drying purpose.

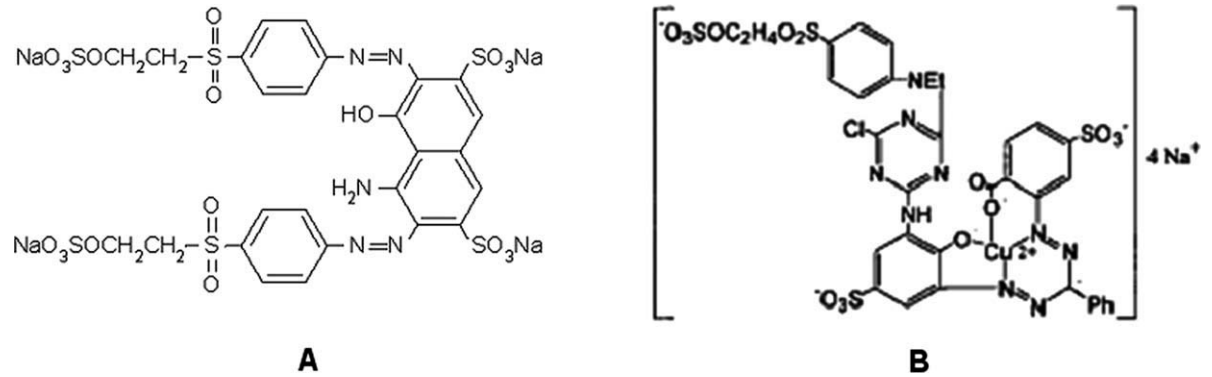

Figure 1 Structure of homo- and hetero-bi-functional reactive dyes, (a) Ramazol Black 5® (C.I. reactive black 5/RB5) and (b) Sumifix Supra Blue BRF® (C.I. reactive blue 221/RB221).

Crosslinking with homo- and hetero-bi-functional reactive dyes

Crosslinking experiments were carried out with both homo- and hetero-bi-functional reactive dyes such as Ramazol Black 5® (C.I. reactive black 5/RB5) and Sumifix Supra Blue BRF® (C.I. reactive blue 221/RB221), respectively. Chemical structures of both reactive dyes are shown in Figure 1. Attachments of β-CD to cotton with both reactive dyes are carried out by the modified 'all in one' method. Dyeing based coupling reaction was carried at fabric to liquor ratio of 1: 40. After the dye bath set out to calculate volume, the dye (3% OWF), electrolyte (NaCl, 50 g/L), β-CD (0–200 g/L), and the cotton fabric (0.7 g) were added to the dye bath. The dye bath was held at 40°C for 15 min for the exhaustion. Sodium carbonate (5 g/L) was then added to the dye bath and the temperature raised to 50°C over a 10 min period, then the NaOH (1*M*) was added and a fixation cycle was run for 45 min. At the end of the fixation cycle, the fabric was removed, rinsed in a warm water to remove any salt. The sample was placed in a water bath at boiling temperature for 20 min to remove any unfixed dye. The samples were rinsed in water and dried in air.

Enzymatic coupling of Tyr-β-CD on cotton surface

β-CD derivative with functional tyrosyl group was especially prepared by Cyclolab® (Cyclodextrin research and development laboratory, Hungary). A Tyr-β-CD has an IUPAC name 6-monodeoxy-6-mono(*N*-tyrosinyl)-β-cyclodextrin. The structure of newly synthesized Tyr-β-CD is given in Figure 2. Synthesis of Tyr-β-CD was confirmed by IR and NMR spectra (not shown). The newly prepared Tyr-β-CD is in zwitterionic form and both cyclodextrin and hydroxyl group of tyrosyl is stable. Tyr-β-CD has a melting point of 244–286°C, giving pH of 5 with 1% solution in water. The solubility of Tyr-β-CD is ~2 g/100 mL of water. UV absorption of Tyr-β-CD shifted when pH is changing from basic to slightly acidic (295 nm at pH 13 to 279 nm at pH 5). Mushroom Tyrosinase (*monophenol monooxygenase*, EC. 1.14.18.1) was purchased from Sigma. It was in the form of lyophilized powder with a ≥1000 unit/mg activity. Tyrosinase mediated enzymatic coupling of specially synthesized Tyr-β-CD on cotton surface was carried out in two steps.

Step 1—Obtaining free and reactive —NH_2 on cotton surface

The procedure involves covalent attachment of reactive dye (RB5) as described in Section "Cross-linking with homo- and hetero-bi-functional reactive dyes" and subsequent reductive cleavage of the dye to get free amine group. Thus, aromatic amines are formed by chemical reduction on cotton with covalently attached reactive dye molecules. The aminization procedure was adopted from Ref. 19. For reductive cleavage of covalently fixed dye was performed in a

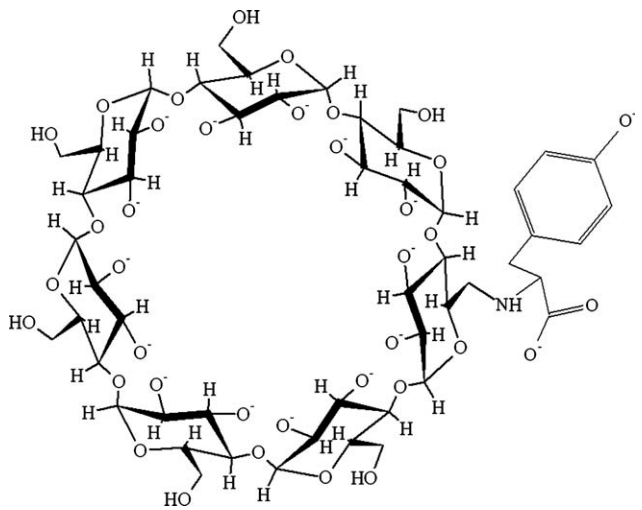

Figure 2 Structure of specially synthesized Tyr-β-CD (6-monodeoxy-6-mono(N-tyrosinyl)-β-cyclodextrin) derivative in zwitterionic form. Tyrosyl group attached to β-CD with amino linkage, having free —OH and —COOH group.

solution of 8 g/L, sodium hydrosulfite ($Na_2S_2O_4$) at 70°C for 2 h. Functionalized colorless fabric sample was then washed in solution of 1 g/L Triton X-100 at boiling temperature for 20 min; rinsed properly in running water and air dried.

Step 2—Tyrosinase mediated coupling of Tyr-β-CD on cotton surface

Tyrosinase mediated coupling of Tyr-β-CD on dyed cotton fabric and reduced cotton fabric were conducted as follows. Initially, experiments were performed in homogeneous system to confirm attachment of tyrosinase and RB5 dye in normal and aminized/reduced form to get free $-NH_2$ groups. Characterization was carried out by analyzing UV-spectra. Actual tyrosinase mediated coupling of Tyr-β-CD on cotton surface was carried out in 0.05*M* sodium phosphate buffer at pH 7.5. Concentration of enzyme tyrosinase was 4000 U, 2 g Tyr-β-CD and the fabric sample weight was 0.7 g. The incubation was conducted at room temperature for 2 h. Samples were washed at 60°C for 30 min and kept for drying overnight. All the experiments were performed in duplicate. Characterization was carried out by analyzing Atomic force microscopy (AFM), scanning electron microscopy (SEM), and β-CD determination by PHP method.

RESULTS AND DISCUSSION

Chemical grafting/crosslinking of β-CD on cotton surface

The porous textile structure hinders free liquid flow, consequently diffusion of β-CD molecules through the pores to the fiber surfaces is a relatively slow process. The diffusion coefficient of uncomplexed cyclodextrin is 3.2×10^{-10} m^2/s.[1] Considering the porosity of the fabric material 0.5, the time needed for β-CD to adsorb at the fiber surfaces is calculated to nearly 8 min. Thus, for all experiments, immersion time for cotton fabric in presence of other grafting/crosslinking agents and β-CD was kept more than 8 min (refer Section "Determination of cyclodextrin contents"). The concentration of β-CD was varied from 0 to 200 g/L for all the experiments. The results for grafting/crosslinking experiments are given in Figure 3. The average standard deviation in the β-CD attached to cotton surface was in between 3 and 6%.

It is clear from Figure 3 that crosslinking with homo-bi-functional reactive dye (RB5) shows maximum attachment. The results shows that increase in β-CD concentration till 70 g/L results into better attachment, above that it reaches a plateau. Other well known techniques, such as grafting with MCT-β-CD and crosslinking with BTCA, show good results in terms of β-CD attachment. However, crosslinking with hetero-bi-functional dye (RB221) shows lowest β-CD attachment among all four techniques. SEM and AFM techniques were used for surface characterization of untreated and diversely treated samples. It is apparent from the AFM images (Fig. 4) that fiber surface have been modified at micro level for (b) MCT-β-CD and (c) RB5 treated samples and confirms the attachment of β-CD on textile surface. As predicted (d) RB221 treated sample shows little surface topographical and color changes compared with blank (a) untreated cotton fiber. No obvious conclusions can be made looking at the SEM pictures (images not shown).

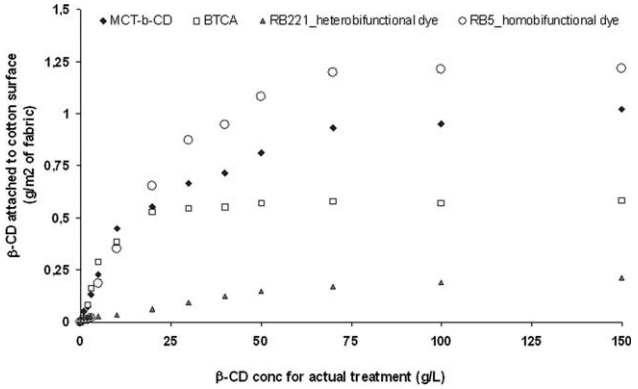

Figure 3 Attachment of β-CD on cotton surface using various chemical grafting/crosslinking techniques.

Mechanism of action for the covalent attachment with MCT-β-CD and crosslinkage with BTCA is described elsewhere.[8,13,14] BTCA—a non formaldehyde crosslinking reagent has four carboxylic acid groups. In presence of catalyst SHPI or heat a cyclic anhydride is formed, that reacts with hydroxyl groups of cellulose and β-CD, forming a stable ester bond.[8] Reactive MCT-β-CD covalently linked to nucleophilic substrates, like cellulose, by a condensation reaction.[13,14] Homo-bi-functional reactive dye, RB5 is a vinyl sulfone dye having two identical vinyl sulfone reactive groups. Hetero-bi-functional dye, RB221 contains two different monochlorotriazine and vinyl sulfone reactive groups. Anchoring β-CD to cotton is a function of the reaction of dye (RB5 or RB221) with β-CD and cellulose molecules. Figure 5 illustrates crosslinking reaction between homo-bi-functional dye (RB5), β-CD, and cotton fiber. The chemical structure of the dye determines its reactivity to both cellulose molecules and β-CD. The hydroxyl groups on the cellulose molecules and β-CD display comparable reactive behavior towards RB5 as seen from the results (Fig. 3). Conversely, crosslinking with RB221 show minimum attachment (Fig. 3). To explain these results, at least four different attachment reaction mechanisms could be proposed between a dye (RB5 or RB221), β-CD, and cotton surface (Cell) as illustrated in Scheme 1.

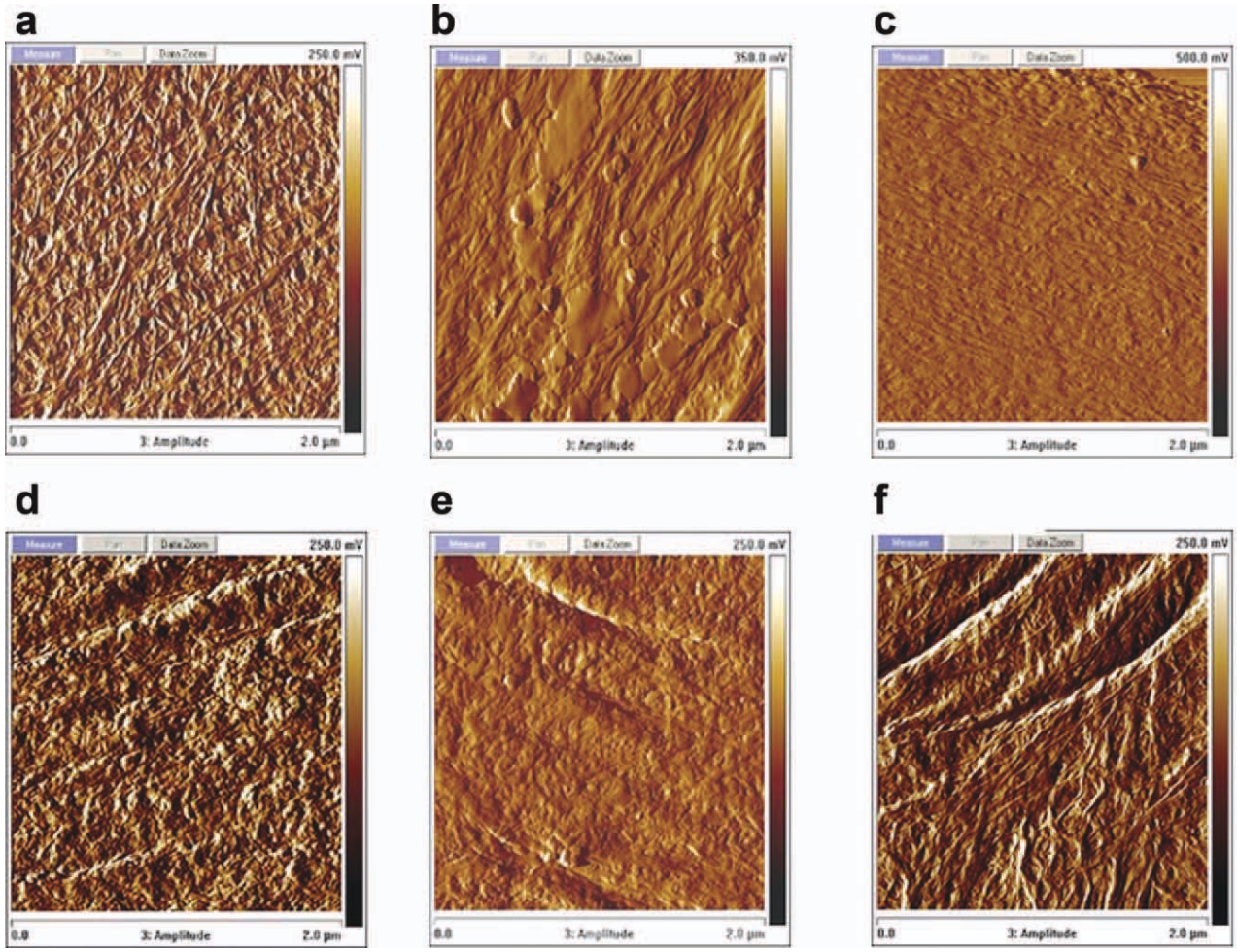

Figure 4 AFM photographs of surface of (a) untreated cotton fabric vs. selected coupling techniques such as (b) reactive MCT-β-CD, (c) Homo-bifunctional dye RB5, and (d) Hetero-bifunctional dye RB221, (e) RB5 + tyrosinase + Tyr-β-CD and (f) RB5 dyed-aminiszed + tyrosinase + Tyr-β-CD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In practice both the dyes (RB5 and RB221) are used for dyeing cotton textiles commercially, that way the reactivity of RB5 and RB221 is already established for Cell-OH. However, the reactivity of RB5 and RB221 has been tested towards β-CD in these experiments. A β-CD molecule can only become anchored to the fiber if one of the reactive groups on the dye is able to react with one of its hydroxyl groups and other with a hydroxyl group on cellulose as illustrated in Scheme 1(a). As illustrated in Figure 3, RB5 mediated coupling shows maximum attachment, hence it can be concluded that the predominant reaction between RB5, β-CD, and cotton surface is similar to Scheme 1(a). This argument is also supported by Chao-Xia et al.[12] However, the attachment reaction for RB221 did not particularly follow dye connected to cellulose and β-CD [Scheme 1(a)]. It seems that attachment reaction for RB221 also followed any of the reaction mechanism as shown in Scheme 1(b–d), in which, both the reactive group of RB221 either have attached to β-CD [Scheme 1(b)] or cellulose molecule [Scheme 1(c)]. An alternative possibility is that a β-CD molecule might be anchored by two dye molecules, forming a longer bridge [Scheme 1(d)]. The treated fabric samples with RB221 and β-CD shows less intense color compared to the RB5 treated samples (personal observation) also supported by Figure 4(d), suggest that the predominant reaction mechanism for RB221 is similar to Scheme 1(c,d).

Tyrosinase mediated coupling

A hypothesis has been proposed for tyrosinase mediated coupling of newly synthesized β-CD derivative with free tyrosyl group (Fig. 2) with cellulose containing free $-NH_2$ groups. To produce new β-CD derivative (Tyr-β-CD), attachment of tyrosyl group to β-CD was carried out via amino group. Hydroxyl and carboxylic group were left free

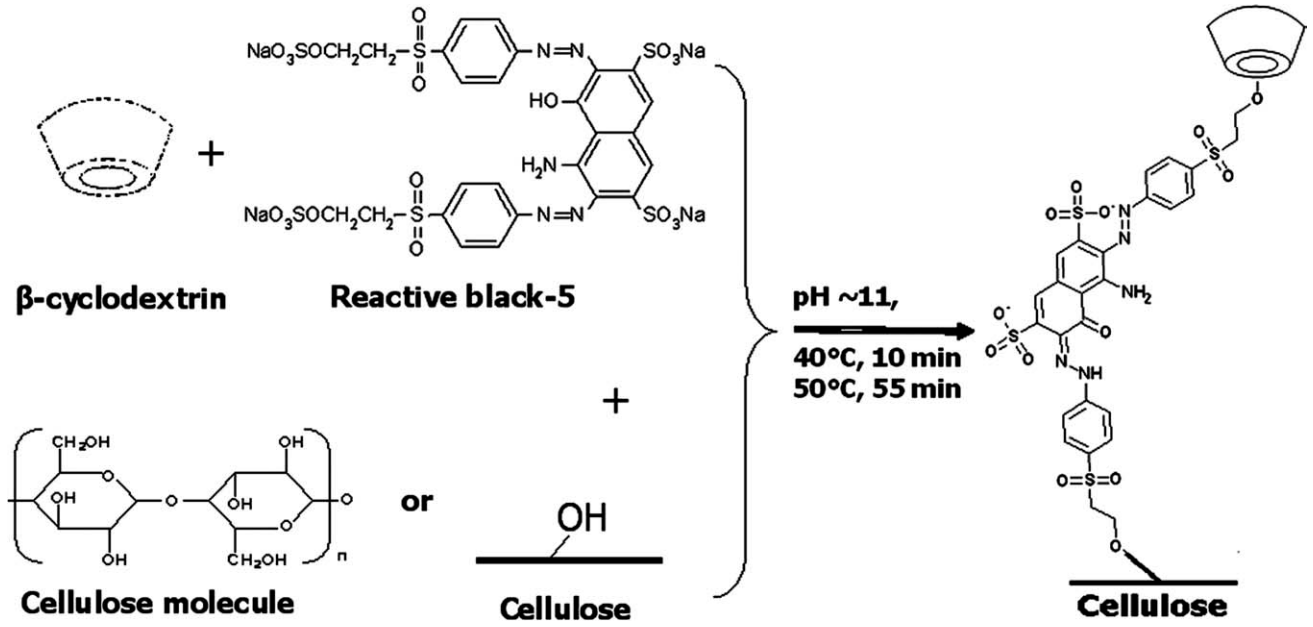

Figure 5 A schematic representation of chemical crosslinking reaction of a homo-bi functional reactive dye (C.I. reactive black 5) as connector between β-CD and cotton substrate.

(Fig. 2) to allow attached tyrosyl undergo reaction with tyrosinase. Tyrosinase is a copper-containing oxidase, which has activity for both catechols and cresols.[20] The enzyme is reported to have two binding sites for aromatic substrates and a different binding site for oxygen-copper.[21] Tyrosinase is responsible for hydroxylation of monophenol to *o*-diphenol (monophenolase or cresolase activity) and then oxidation of diphenol to highly reactive *o*-quinones (diphenolase or catecholase activity).[22] More specifically, in nature, tyrosinase converts tyrosine to L-dopa (diphenol) and then to dopaquinone (reactive *o*-quinones). Subsequently the free $-NH_2$ of dopaquinone undergoes cyclic reaction to form Leukodopachrome which is essentially indole moiety.[22] To avoid this later step (cyclization to Leukodopachrome), precautions have been taken while synthesizing for not having free $-NH_2$ group on Tyr-β-CD (Fig. 2), so that reactive *o*-quinones group can undergo with permanent coupling with available free $-NH_2$ on cotton surface via Schiff base reaction

Cell—O—Dye—O—β-CD [a]

Cell—O—Dye—O—Cell [b]

β-CD—O—Dye—O—β-CD [c]

Cell—O—Dye—O—β-CD—O—Dye—O—Cell [d]

Scheme 1 Proposed possible reaction mechanism between a Dye (RB5 or RB221), β-CD, and cotton surface (Cell).

leading to covalent fixation of Tyr-β-CD on modified cotton substrate. Figure 6 schematically illustrates a two step proposed mechanism of tyrosinase mediated coupling of Tyr-β-CD to dye with RB5 and aminized cotton surface (refer Section "Chemical fixation of β-CD on cotton surface" for the procedure).

Tyrosinase mediated coupling of Tyr-β-CD to RB5 dye in homogenous system

To confirm the proposed reaction as illustrated in Figure 6, experiments were conducted in homogenous system. Two sets of experiments were performed in which attachment between a dye (RB5) containing one free $-NH_2$ group and Tyr-β-CD confirmed via UV–vis spectroscopy. Four different UV–vis spectra were made for the following samples, (a) only dye RB5, (b) only Tyr-β-CD, (c) RB5 + Tyr-β-CD + deactivated tyrosinase, (d) RB5 + Tyr-β-CD + tyrosinase. Figure 7 shows all four spectra; there is clear difference between spectra for sample C and D. Spectra D shows increase in absorbance at wider wavelength (280–520 nm), confirms the tyrosinase catalyzed attachment of RB5 and Tyr-β-CD. Similar four spectra for Set II have been performed, the only difference is reduced (aminized) RB5 to get aromatic $-NH_2$ groups (Step 1, Fig. 6). Spectra for aminized dye (RB5) is different from normal RB5 dye (sample A, Set II vs. Set I in Fig. 7), in terms of missing peak at 600 nm, owing to absence of chromophoric group. An overall increase in absorbance was observed for sample D at 330–500 nm, when tyrosinase was brought in contact with aminized RB5 dye and Tyr-

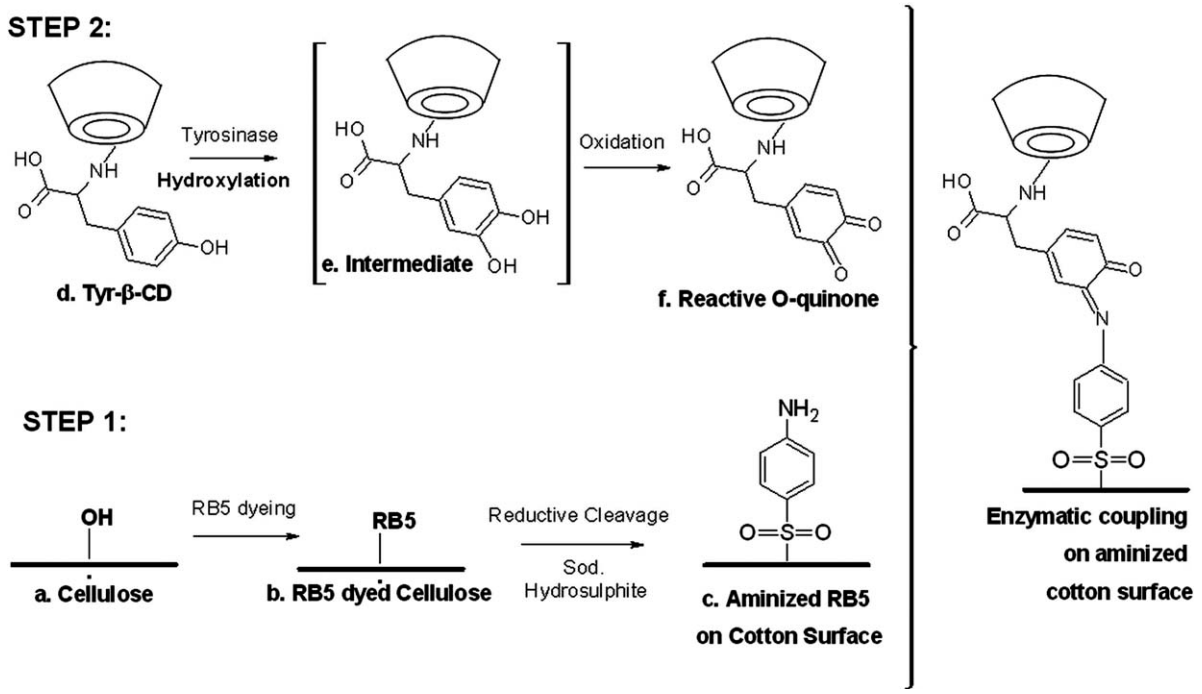

Figure 6 A systematic illustration of tyrosinase mediated (enzymatic) coupling of Tyr-β-CD to reactive black 5 dyed and aminized cotton surface.

β-CD. All results are shown in Figure 7 (Set II), are in line with earlier results, reconfirms tyrosinase mediated attachment of aminized RB5 to Tyr-β-CD.

Tyrosinase mediated coupling of Tyr-β-CD to cotton surface

Owing to limited availability of Tyr-β-CD sample, experiments could not be conducted at various concentrations as performed for chemical grafting/crosslinking. Four selected samples were prepared, (a) Tyr-β-CD + tyrosinase + RB5 dyed cotton fabric, (b) blank for sample 'a' without tyrosinase, (c) Tyr-β-CD + tyrosinase + RB5 dyed and aminized fabric and (d) blank for sample 'c' without tyrosinase. As shown in Figure 8, Tyr-β-CD attachment is maximum for RB5 dyed and aminized fabric (sample 'c'). Enzymatic coupling for sample 'a' is much lesser than the sample 'c' (0.07 g/m^2 compared to 0.17 g/m^2). It can be attributed to better coupling possibilities of reactive *o*-quinones (Dopaquinone) to aromatic $-NH_2$ groups (sample 'c') over nonaromatic $-NH_2$ group (sample 'a'). As predicted, both the blank treatments (sample 'b' and 'd') without tyrosinase show almost no attachment. A comparison have made between overall attachment for sample 'a' and 'c' was with other chemical grafting/crosslinking techniques for similar concentration of β-CD

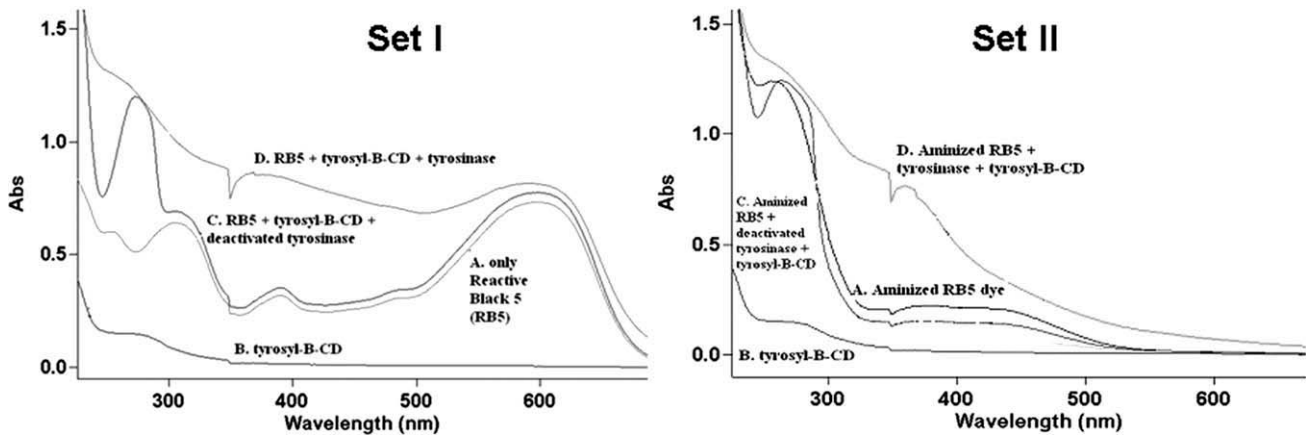

Figure 7 UV–vis spectra showing tyrosinase mediated coupling of Tyr-β-CD in homogeneous system. Set I—Reactive black 5 (RB5) having one free $-NH_2$ group and Set II—an aminized RB5 having free aromatic $-NH_2$ group.

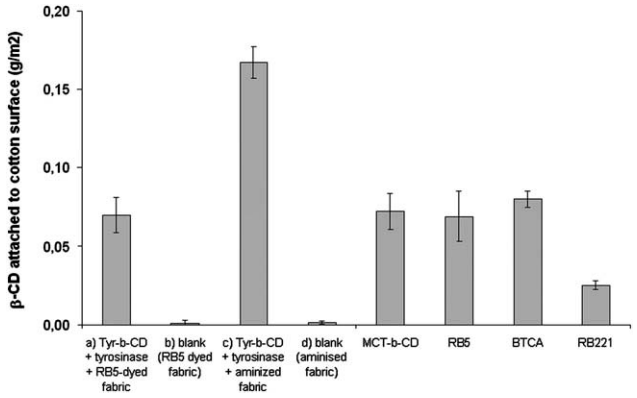

Figure 8 Tyrosinase mediated coupling of Tyr-β-CD on cotton surface (both RB5 dyed fabric and RB5 dyed-aminized fabric) and its comparison with other chemical grafting/crosslinking techniques.

used in experiments (2 g/L). It is clear from the Figure 8 that, attachment for sample 'c' is more than double for any of the chemical grafting or crosslinking techniques. This proves the superiority of the enzymatic coupling techniques which was performed at ambient conditions.

SEM and AFM images were made to observe any surface changes at the microscopic level (Fig. 4). AFM images of blank (untreated cotton sample 'a') are compared with tyrosinase mediated coupling on RB5 dyed [Fig. 4(e)] and RB5 dyed-aminized [Fig. 4(f)] cotton surface. No obvious interpretation could be possible from the SEM images (images not shown). It is clearly seen that tyrosinase mediated coupling of RB5 dyed cotton fabric [Fig. 4(e)] makes surface smoother compared to untreated cotton sample, in which criss-cross pattern of cellulose microfibril are visible. Aminization of dyed RB5 fabric followed by enzymatic coupling [Fig. 4(f)] again unveils the criss-cross pattern of cellulose microfibrils which was covered because of chromophoric group of RB5 dye. This observation is owing to aminization reaction rather than of tyrosinase treatment. The resulted surface, however, still looks much smoother compared to untreated cotton.

CONCLUSIONS

Five different techniques were evaluated for connecting host systems (β-CD) to cotton textile surface. Crosslinking between β-CD and cotton surface with homo-bi-functional reactive dye (RB5), and grafting with MCT-β-CD shows overall maximum attachment among all chemical based techniques. A new derivative of cyclodextrin called Tyr-β-CD (6-monodeoxy-6-mono(*N*-tyrosinyl)-β-cyclodextrin) was specially synthesized to realize enzymatic coupling. Tyrosinase mediated enzymatic coupling was first evaluated in homogenous system with reactive black 5 dye and aminized dye. Coupling was confirmed by UV-spectroscopy. Finally, enzymatic coupling experiments were conducted with RB5 dyed fabric and RB5 dyed-aminized fabric. At specific Tyr-β-CD concentration (2 g/L) tyrosinase mediated coupling on RB5 dyed and aminized fabric shows superior results than all other techniques evaluated in this study. In nutshell both newly developed crosslinking technique (RB5) and tyrosinase mediated enzymatic coupling techniques are superior and unique compared to two well established grafting techniques (BTCA and MCT-β-CD).

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