

Grafting of Cotton Fiber by Water-Soluble Cyclodextrin-Based Polymer

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ABSTRACT: β -cyclodextrin (CD)-based linear water-soluble polymers were synthesized in a controlled manner by a one-pot synthesis method. The synthesized water-soluble polymer was covalently fixed onto cotton surfaces by a polycondensation reaction at controlled conditions. Grafting on cotton fibers transfers the cyclodextrin properties onto its surface. The grafting occurred through the formation of a crosslink between hydroxyl groups of cotton and CD polymer. This was confirmed using FTIR spectroscopy, DSC, tensile strength, computer color matching, and solvent fastness analysis. The tensile strength of modified fiber samples was

unchanged as compared to that of unmodified fiber samples. The percentage of grafting depended on a number of parameters and specifically on (i) temperature, (ii) time, and (iii) pH of the reaction medium. Similarly, under optimum conditions the weight increase on cotton fabric due to the grafting reaction could reach 10–15 wt %. The grafted cotton fabric shows good dyeability and solvent fastness properties. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2056–2061, 2009

Key words: β -cyclodextrin; water-soluble polymer; grafted cotton; polycondensation

INTRODUCTION

Grafting of water-soluble cyclodextrins on cotton surfaces has received attention for modern textile applications.¹ Through the grafting process, the torus shaped cyclodextrins and their derivatives can be immobilized on the textile surfaces.² Cyclodextrins (CDs) are essentially composed of α -1, 4-linked D (+)-glucopyranose polysaccharides. Because of the ring formation, they have a hydrophobic cavity that can give host-guest inclusion compounds with a number of unique hydrophobic molecules.^{3,4} These inclusion compounds can be used in different areas like cosmetics, pharmaceuticals, analytical chemistry, and in textile applications.⁵

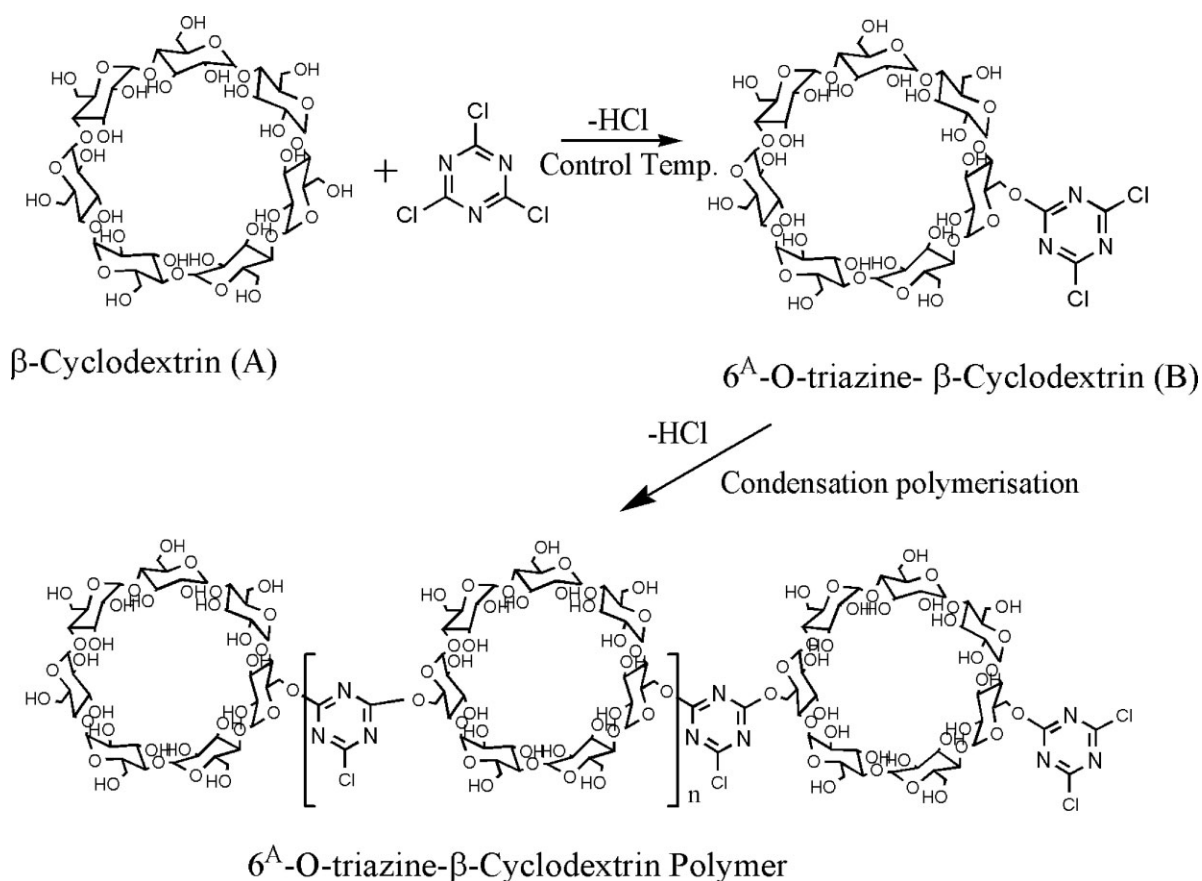
The modification of natural fiber with CDs is being used in modern textile processing. During the late 1980s some work on grafting of modified CDs onto cotton fiber has been reported.^{6–9} Many of the papers and patents report the use of CDs for antibacterial, insect-free, aroma finishing and the textile finishing applications.^{10–12} One of the many applications of CDs in textiles is to either capture the unpleasant smells due to perspiration, or to promote

the controlled release of perfumes.¹³ A number of reports are available that describe the grafting of CDs onto natural and synthetic fibers.^{14–16} Szejtli et al. prepared CD grafted cellulose fibers by condensation reaction, where cyclodextrin was grafted onto cotton surface by polycondensation reaction using epichlorohydrin as a crosslinking agent.¹⁷ In 1996, Denter et al. modified the surface of the synthetic and natural fibers with cyclodextrin using cyanuric chloride as a crosslinking agent.¹⁸ Martel et al. grafted CDs onto polypropylene fabrics and wool fibers by electron beam techniques and using polycarboxylic acids (PCA) as crosslinking agents.¹⁹ Anderson et al. reported that an azo dye rotaxane when attached to the cellulose surface through a suitable linker enhances the stability of azo dye towards reductive bleaching. This has been due to a stable azo dye rotaxane encapsulation.²⁰ Thus, these modified textile materials have a number of advantages like enhancing the fiber wettability, increasing the fiber surface energy and providing higher dyeing abilities. In most of these reports pristine cyclodextrins were grafted onto the fibers using a suitable crosslinking agent.²¹

In this work, we report the synthesis of a water-soluble β -cyclodextrin chain polymer and its subsequent crosslinking on to cotton surface. The overall objective was to establish that a CD-based polymer could be covalently bound to cotton fiber or yarn or fabric using a polycondensation reaction at controlled condition that increased the stability of the

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Scheme 1 Synthetic scheme for the reaction between β -cyclodextrin and cyanuric chloride.

azo dye after dyeing. The covalently grafted cotton was characterized by FTIR spectroscopy, TGA, DSC, and single yarn strength analysis.

EXPERIMENTAL

Cotton yarn, fiber and fabric (Shivna Spinners, Indore) were washed with boiling aqueous Na_2CO_3 for 3 h and dried under ambient conditions prior to treatment. β -cyclodextrin was obtained from Signet Chemical Corporation (Mumbai, India.) as a gift sample and was used as received. Cyanuric chloride and other chemicals were purchased from local market and used without further purification.

Synthesis of β -cyclodextrin polymer grafted cotton yarns, fibers and fabrics

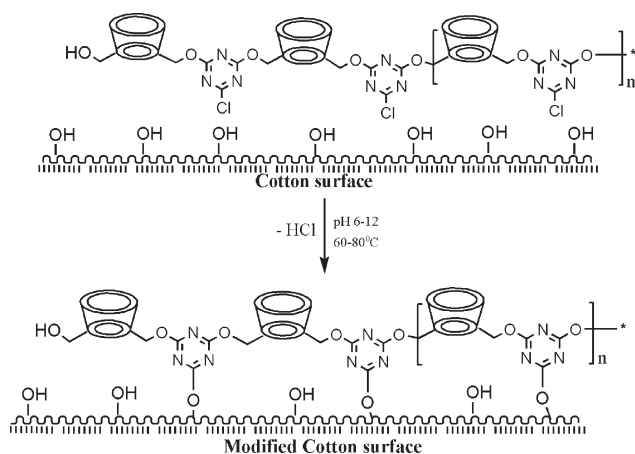
Synthesis of 6^A-O-triazine crosslinked- β -CD polymer

In the reaction scheme a 1 : 1 mol ratio of β -CD and cyanuric chloride were taken in two flasks and dissolved separately in required amount of distilled water at controlled pH. The hydrolysis of cyanuric chloride was prevented by suitable adjustment of pH. In a typical reaction, β -CD solution of predeter-

mined pH was taken into a round bottom flask and kept in ice bath with continuous stirring and the required temperature maintained. To this the cyanuric chloride solution was added drop wise with the help of pressure equalizing funnel into the β -CD solution maintaining the temperature. After addition, the reaction was continued for 4 h. Stirring was continued for another 12 h while the contents were allowed to attain ambient temperature (30°C). The neutralized product was dialyzed for 24 h using a dialysis membrane of molecular weight cut off of 3500 and freeze-dried to get an off-white fluffy product ($M_w = 5680$ by ESI). The typical reaction is shown in Scheme 1. This polymer was used directly for grafting on to cotton fiber, yarn and fabric.

Grafting

Grafting on to the cotton was performed in a two-necked reactor equipped with a stirrer and a thermometer jacket. The typical reaction is shown in Scheme 2. Approximately 0.5 g of pretreated cotton yarn/fiber/fabric was taken in required amount of distilled water at controlled pH (6–12 pH) using 0.1N NaOH solution. 0.5 g of the synthesized CD



Scheme 2 Synthetic scheme for the grafting of cotton with β -cyclodextrin.

polymer was added to it under constant stirring. After addition, the reaction was continued and temperature maintained between 60°C and 80°C for 12 h. After that the grafted samples were dried at 80°C for 4 h under vacuum and washed several times with water to remove any ungrafted polymer from the cotton surface and finally washed with methanol and dried at 80°C under vacuum to a constant weight. The grafting % was calculated by the following equation.

$$\text{Grafting \%} = 100 \times \frac{(\text{Weight of grafted cotton} - \text{Weight of ungrafted cotton})}{\text{Weight of ungrafted cotton}}$$

Dyeing process of cotton fabric (grafted and ungrafted) with β -naphthol azo dye

One gram each of grafted and ungrafted cotton fabric was dipped in a 20% solution of β -naphthol in NaOH separately. They were then removed after 10 min and the excess solution was dripped off. One gram of *p*-nitroaniline was dissolved in 2 mL HCl and mixed with 1 g of NaNO₂ in a beaker kept in an ice bath maintained at 0°C. The cotton fabric coated with β -naphthol was then dipped in this beaker when an orange dye was formed. The fabric was left as it is for about 30 min and then removed for washing. The dyed fabric was washed several times till there was no color removal from the fabric and dried in an air oven.

Analysis

FTIR spectroscopy

Infrared spectra of CD polymer grafted cotton, β -CD polymer, and β -CD were taken on an FTIR spectro-

photometer (Perkin-Elmer, 1725) from their KBr pellets and scanned at 4 cm⁻¹ resolution over the range 4000–400 cm⁻¹ in the transmission mode.

X-ray diffraction

X-ray powder diffraction pattern of the polymer sample was taken on RIGAKU-DMAX-2200 instrument over the range 5–50° at a scan rate of 2° min⁻¹ using CuK α radiation monochromatized with a graphite crystal.

Thermal analysis

The TGA of the synthesized β -CD polymer was taken on a Shimadzu TGA-50 system with a heating rate of 10°C/min.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) scans were taken on a Mettler (Toledo-822) differential scanning calorimeter. The DSC scans of cotton fiber and β -CD polymer grafted cotton fiber were obtained from samples that were packed into aluminum pans and heated at rate of 10°C/min.

Computer color matching analysis of cotton fabric after dyeing

Computer color matching analysis was carried out using UV-Vis spectrophotometer premier color scan instrument with the following Kubelk-Munk relation [eq. (1)].

$$F(R) = (1 - R)^2 / 2R = k/S \quad (1)$$

where, k = Absorption Coefficient and S = Scattering Coefficient.

Color fastness of the cotton fabric (grafted and ungrafted) against solvent

Ungrafted and grafted cotton fabric after dyeing were immersed in a fixed amount of ethanol solution and the samples were stored at room temperature in a closed vessel for 24 h. The dye fastness was calculated from the removal of dye by taking the UV-Vis absorbance of the solution.

RESULTS AND DISCUSSION

Grafting of the water-soluble polymer depended on the time of the reaction. Initially the percentage of polymer grafting increased with time but remained constant subsequently. We observed that 10–12 h duration was the optimum time for the grafting process. Table I gives the effect of the pH on the

TABLE I
Variation of Grafting Percentage at Different Ph

S. No.	pH	% of Grafting
1	12	15
2	11	14
3	10	15
4	9	15
5	8	14
6	6	12

grafting process. We observed that the percentage of CD-polymer grafted onto cotton fiber/yarn/fabric depends on the pH of the reaction medium. The pH was varied from 6 to 12 and at each pH five sets of reactions was carried out and the percentage grafting calculated. These data show that there is only a minor change in % grafting as the pH is increased from 6 to 12. After the completion of grafting reaction, the treated cotton was dried at different temperatures (5 sets of treated cotton yarns were dried at different temperatures for calculating the % grafting and the average breaking strength measured). These values are reported in Table II. The results show that the chemical grafting with β -cyclodextrin polymer on cotton yarn surface does not significantly damage the cotton yarn. Here, we observed that due to the temperature variations in drying, no significant changes were observed in percentage of elongation.

Figure 1(inset) shows the FTIR spectra of β -CD and β -CD-polymer in which the specific absorption peaks are at 3421 cm^{-1} (OH stretching H-bonded), 2927 cm^{-1} (C—H stretching), 1724 cm^{-1} (C=N stretching), 1612 cm^{-1} (OH bending), 1384 cm^{-1} (OH deformation), 1243 cm^{-1} (OH bending), 1157 cm^{-1} (COC stretching and OH bending), 1080 and 1029 cm^{-1} for (COC Stretching) characteristic of 6^A -O-triazine- β -CD polymer together with the peak at 3382 cm^{-1} (OH stretching H-bonded), 2927 cm^{-1} (C—H stretching), 1643 cm^{-1} (OH bending), 1369 cm^{-1} (OH deformation), 1245 cm^{-1} (OH bending), 1157

TABLE II
Variation of the Average Breaking Strength on the % Grafting

S.No.	Cotton yarn	% Grafting	Average breaking load (g)	% Elongation
1	Untreated	0	635	6
2	Treated Set-1	14	643	8
3	Treated Set-2	14	630	8
4	Treated Set-3	14	611	7

Gage length: 10 cm.

Set-1: Treated cotton yarn dried at 80°C .

Set-2: Treated cotton yarn dried at 70°C .

Set-3: Treated cotton yarn dried at 60°C .

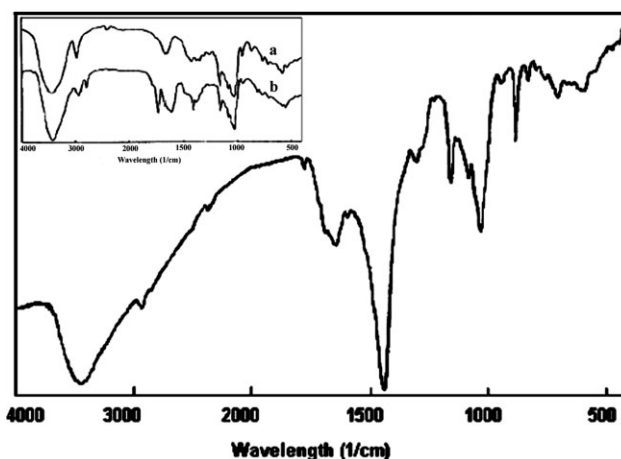


Figure 1 FTIR spectra of β -CD-polymer grafted cotton fiber (Inset FTIR spectra of (a) β -CD and (b) 6^A -O-triazine- β -CD polymer).

cm^{-1} (COC stretching and OH bending), 1080 and 1029 cm^{-1} for (COC Stretching) of β -CD. The absorption band at 1724 cm^{-1} of 6^A -O-triazine- β -CD polymer indicates that C=N stretching comes from triazine ring that indicate triazine linkage takes place between the β -cyclodextrin. The FTIR of β -CD-polymer grafted cotton fibers is shown in Figure 1. The characteristic absorption band show the specific peaks at 3448 cm^{-1} (OH stretching H-bonded), 2923 cm^{-1} (C—H stretching), 1774 cm^{-1} (C=N stretching), 1639 cm^{-1} (OH bending), 1442 cm^{-1} (OH deformation), 1303 cm^{-1} (OH bending), 1157 cm^{-1} (COC stretching and OH bending), 1083 and 1029 cm^{-1} (COC stretching). The presence of C=N group on the β -CD-polymer grafted cotton fiber indicates that β -CD-polymer has been successfully grafted onto cotton fiber.

The X-ray diffraction pattern of the synthesized β -CD polymer is shown in Figure 2. The synthesized polymer does not have the typical 2θ (9 , 12.5 , 19.6 , 23.0 , 27.0 , and 34.8°C) values of the parent β -CD. This XRD data shows that the β -CD is modified due to the condensation reaction thus losing its crystallinity.

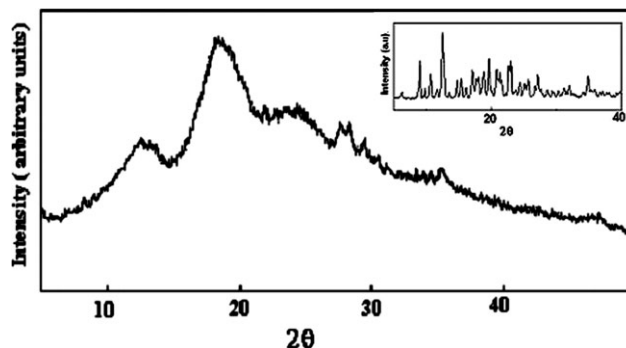


Figure 2 XRD of the β -CD-polymer and β -CD (inset).

The TGA thermograms are shown in Figure 3. β -cyclodextrin shows mass loss in three different temperature regions. The first mass loss at around 107°C is due to the loss of moisture, the second and third mass loss at 300°C and 367°C due to a start of melting and decomposition of glucose unit in β -CD. However, in case of the β -CD polymer the thermogram is different with the first mass loss at around the same temperature but second mass loss is at a lower temperature of 248°C due to the modification of the cyclodextrin unit with the resulting loss of the crystalline nature of the cyclodextrin molecule. Subsequent loss occurs due to the decomposition of the glucose and triazine linker.

Differential scanning calorimetry (DSC) gives significant information shown in Figure 4. The β -CD polymer grafted cotton exhibited endothermic transition at around 150°C (glass transition temperature of β -CD chain polymer). Whereas ungrafted cotton did not exhibit any exothermic and endothermic transition at that temperature. A new endothermic transition in the β -CD polymer grafted cotton was observed which is probably due to the enhancement of interaction between hydroxyl groups of grafted β -CD polymer and the hydroxyl groups in the cotton fiber backbone. This further confirms that grafting has occurred on the cotton fiber.

The Spectra-scan computer color matching system analysis indicates the average k/S values of the cotton fabric (ungrafted and grafted with the water-soluble polymer) after dyeing with the azo dye. The grafted cotton fabric shows the higher (1.66) k/S value (average) compared with the ungrafted cotton fabric (1.54). These results suggest that the grafted cotton fabric contains more dye on the cotton surface compared to the ungrafted cotton fabric after the dyeing. The water-soluble polymer grafted cotton fabric also showed better solvent fastness properties compared to the ungrafted cotton fabric after dyeing. Results show that after 24 h, the water-soluble

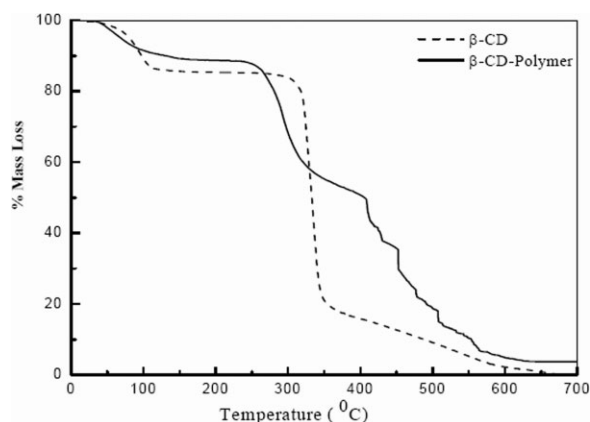


Figure 3 TGA of β -CD- polymer and β -CD.

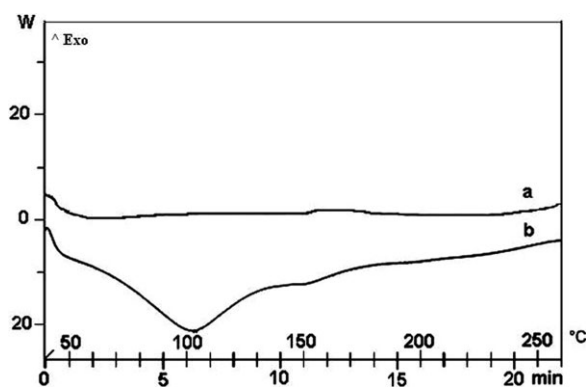


Figure 4 DSC of β -CD-polymer grafted cotton (b) and ungrafted cotton (a)

polymer grafted cotton fabric has 66% more dyeability than the ungrafted cotton fabric.

CONCLUSIONS

Cotton yarn, fiber, and fabric were successfully grafted with β -cyclodextrin polymer, to obtain inclusion compounds with suitable hydrophobic species immobilized on the cotton surface. Single yarn strength testing showed that no surface property deterioration happened due to the chemical treatments of the cotton yarn, fiber and fabric. In this work, we have transferred the β -cyclodextrin properties on cotton through the grafting technique. Water-soluble β -cyclodextrin polymer grafted on the cotton surface enhanced the dyeability and solvent fastness properties due to the increased stability of cyclodextrin encapsulated dyes. This grafted cotton can be used in various applications, for instance, intelligent clothing fabrics and filter materials.

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