

# Polycarboxylic Acids as Crosslinking Agents for Grafting Cyclodextrins onto Cotton and Wool Fabrics: Study of the Process Parameters

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Received 25 July 2000; accepted 24 July 2001

**ABSTRACT:** In this paper we describe a new method for the grafting of cyclodextrins (CDs) onto cotton or wool fabrics. The novelty principally concerns the chemical approach of the grafting reaction that was carried out in the presence of polycarboxylic acids, such as 1,2,3,4-butanetetracarboxylic acid, citric acid, or polyacrylic acid. All types of native or CD derivatives could be used successfully as long as they carried enough remaining hydroxyl groups. For example, the amount of native  $\beta$ -CD fixed onto the fabrics increased up to 12% in weight, whereas this value decreased to only 3% for the randomly methylated derivative of  $\beta$ -CD (RAMEB). We observed that phosphorous salts, such as sodium mono- and dihydrogen phosphate or sodium dihydrogen hypophosphite, catalyzed the reaction. On the other hand, the conventional and convenient pad-dry-cure technique that is currently used at the industrial scale in textile processing was applied. We report that the polycarboxylic acids play the role of linking agent through an esterification (or amidification) reaction with the OH (or  $\text{NH}_2$ ) groups of both CD and cotton (or wool) fibers. In addition, this reaction could lead to the graft of a copolymer formed between CD and the polycarboxylic acid. The reaction yield depends on the concentration and nature of the aforementioned reactants and catalysts and on the curing conditions (time and temperature). © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1449–1456, 2002

**Key words:** cyclodextrins; textile finishing; grafting; cellulose; cotton; wool; citric acid; polyacrylic acid; 1,2,3,4-butanetetracarboxylic acid

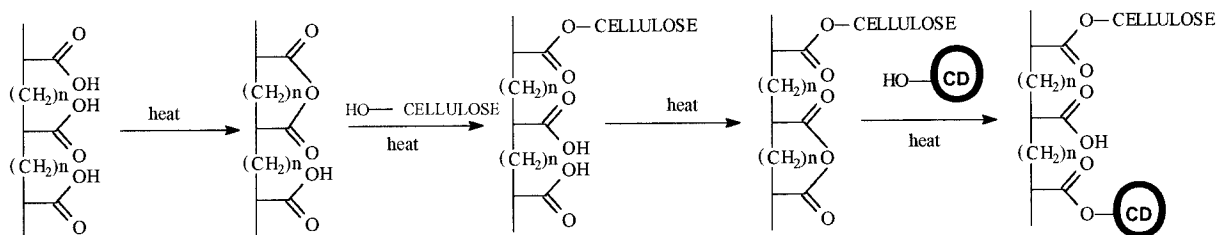
## INTRODUCTION

Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides made of six, seven, or eight glycosidic units linked by  $\alpha(1\rightarrow4)$  bonds and are called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD, respectively. The hydrophobic internal cavity and the hydrophilic external part of

this molecular structure are antagonist features that are at the origin of the original properties of and scientific interest in CDs.<sup>1</sup> This product, issued from enzymatic degradation of starch, has the capability to make inclusions (or host-guest) compounds with aliphatic and especially aromatic molecules. Among the possible applications of CDs, encapsulation of active substances, such as flavoring agents, fragrances, pesticides or drugs,<sup>2</sup> is often reported. Such supramolecular compounds are of interest because they increase the

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*Journal of Applied Polymer Science*, Vol. 83, 1449–1456 (2002)  
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DOI 10.1002/app.2306



**Scheme 1** Grafting reaction of cyclodextrin onto cellulose by the intermediate of a polycarboxylic acid bearing more than three carboxylic functions.

solubility of the guest in aqueous media, protect the guest against oxidation and thermal or chemical degradation, and prevent rapid evaporation of the guest.<sup>3</sup>

The impregnation or covalent binding of CDs onto textile can assign to the latter the aforementioned complex-forming ability of CDs and can offer some new types of applications to the modified fabrics. Such a purpose was first reported by Szejtli et al. who grafted CDs onto cellulose using epichlorohydrin as a crosslinking agent.<sup>4,5</sup> Then, Poulakis et al. reported the physical or chemical incorporation of CDs into natural or synthetic matter.<sup>6</sup> CD derivatives, such as a monochlorotriazinyl  $\beta$ -CD derivative, have been fixed permanently onto different polymer materials, including fibers, by Denter et al.<sup>7</sup> and Reuscher et al.<sup>8</sup> Finally, we also recently reported an original method for the grafting of CDs onto polypropylene fabrics using electron beam technology.<sup>9,10</sup>

Furthermore, in another recent study, we have proposed the possibility of fixing CD permanently to textile fibers, thanks to the use of polycarboxylic acids as crosslinking agents.<sup>11,12</sup> The purpose of this paper is to present some details of this work.

The method has been adapted from that reported by Welsh et al.<sup>13</sup> for the nonformaldehyde durable press finishing of textile. It consists of the crosslinking of cellulosic fibers by polycarboxylic acids (PCAs) in the presence of phosphorous catalysts. The reaction occurs by dehydration below the curing temperature of the PCAs, which yields a cyclic anhydride intermediate that readily reacts with the hydroxyl groups of cellulose by esterification. Then, two of the remaining carboxylic groups of the reacted PCAs can form a second anhydride that can also react with another cellulose unit from another macromolecular chain. This reaction scheme (Scheme 1) was made possible when PCAs containing least three carboxylic groups spaced from one or two intermediate at-

oms were used. This crosslinking reaction of the fibrous network led to the desired mechanical properties of the fabric.

In our approach, CDs were mixed with PCAs in the impregnating solution so that the latter could react with both CD and fibers. This paper describes the study of the parameters involved in this finishing process. These parameters include the curing conditions (temperature, time), the nature and concentration of the catalysts (sodium mono- and dihydrogen phosphate and sodium dihydrogen hypophosphite), the PCAs [1,2,3,4-butanetetracarboxylic acid (BTCA), citric acid (CTR), and polyacrylic acid (PAA)], the native  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD, and the randomly methylated derivative of  $\beta$ -CD (RAMEB).

## METHODS AND MATERIALS

### Methods

A ternary aqueous solution containing the PCA (0–100 g/L), a phosphorous catalyst (0–60 g/L), and CD (0–150 g/L) was prepared. All fabric samples (16.5 × 32 cm), before and after treatment, were oven dried at 104 °C for 1 h, placed into a dessicator for 30 min, and immediately weighted. The fabric was impregnated with the aforementioned solution and padded; the wet pick up was 100 ± 1% for both cotton and wool. The fabric was then mounted on a pin frame and oven dried at 90 °C. Curing occurred at the desired temperature and time during a second passage in the oven. Samples were then abundantly washed with hot (60 °C) distilled water, spin dried, oven dried (104 °C), and weighed. The weight gain of the fabrics (symbolized by %wt) was measured to evaluate the yield of the grafting reaction; the following equation was used:

$$\% \text{ wt} = \frac{(m_f - m_i)}{m_i} \times 100 \quad (1)$$

where  $m_i$  and  $m_f$  are the weight of the sample before and after treatment, respectively. Most of the experiments were performed in triplicate, and the precision of the value of %-wt was estimated as  $\pm 1.5$  percent units.

It is worth noting that the limiting factor caused by the low solubility of  $\beta$ -CD (only 18 g/L at 20 °C) was resolved because of the solubility promoting effect of the PCAs that were also contained in the aqueous solution.<sup>14,15</sup> As a consequence,  $\beta$ -CD could be absorbed and grafted onto the fabrics in the same range of magnitude as the other CDs (that have a natural higher solubility).

## Materials

Cotton print cloth, bleached, mercerized (Test Fabric 400M 100g/m<sup>2</sup>) was used throughout the study. Virgin woven wool had a surface weight of 120 g/m<sup>2</sup>. The 1,2,3,4-Butanetetracarboxylic acid, citric acid hydrate, and polyacrylic acid ( $M_w = 2000$ ) that were used as crosslinking agents and the  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , and  $\text{NaH}_2\text{PO}_2 \cdot x\text{H}_2\text{O}$  that were used as catalysts were from Aldrich Chemicals (Milwaukee, WI).  $\alpha$ -,  $\beta$  and  $\gamma$ -CD and RAMEB (randomly methylated  $\beta$ -CD) were gifts from WACKER GmbH (Munich, Germany). RAMEB is a  $\beta$ -CD whose 13 (on average) out of 21 hydroxyl groups have undergone a methylation reaction (determined by mass spectrometry).

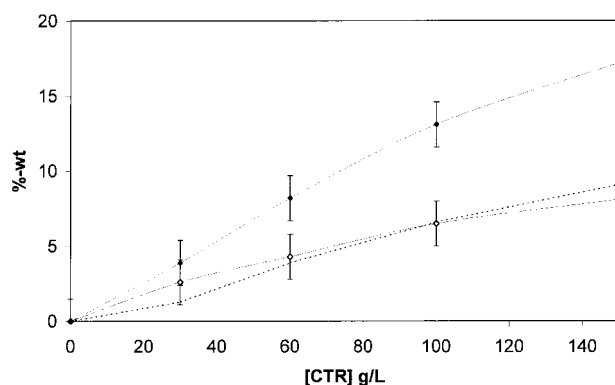
The textile finishing equipment (ERNST BENZ AG, Switzerland) consisted of a two-roll padder (pressure 1.5 kp/cm, speed 1.5 m/min) and a curing oven equipped with a mechanical circulation of air. The sample was set onto a pin frame and circulated at a determined speed into the oven (length = 1.8 m).

A Fourier transform infrared (FTIR) study was carried out by the transmission method (KBr pellets) with a Perkin Elmer Spectrum One spectrometer.

## RESULTS AND DISCUSSION

### Evidence of the Grafting Reaction

The crosslinking of cotton by CTR (open symbols) is accompanied by an increase of the %-wt of the cotton fabric versus the concentration of the latter in the impregnating bath, as shown in Figure 1. This result can be easily explained by the fact that CTR is grafted onto the fibers by the esterification



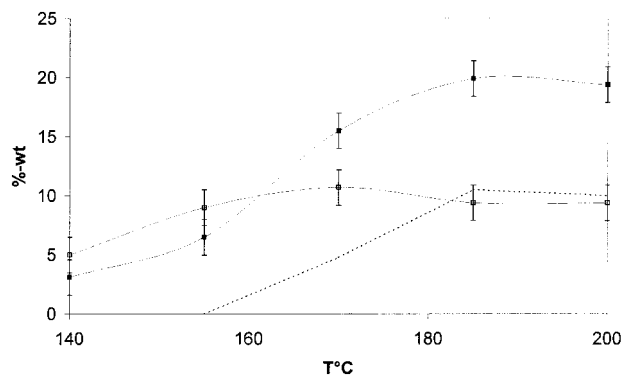
**Figure 1** Weight increase of the cotton fabrics padded and cured with [CTR] = 60 g/L or  $[\text{NaH}_2\text{PO}_4, \text{H}_2\text{O}] = 30\text{g/L}$ . Key: (open symbols)  $[\beta\text{-CD}] = 0\text{ g/L}$ ; (solid symbols)  $[\beta\text{-CD}] = 100\text{ g/L}$ ; (dashed curve) calculated amount of fixed CD.

reaction described by Welsh.<sup>16</sup> On the other hand, in experiments carried out in the presence of  $\beta$ -CD (fixed to 100 g/L) and various concentrations of CTR (full symbols), it was observed that the %-wt of the sample was superior. As a consequence, the amount of CD immobilized on the fabrics could be evaluated by the difference between the aforementioned curves, as represented by the dashed curve in Figure 1.

It is worth mentioning that the grafting reaction occurred by a reaction between PCA and CD on one hand, and between PCA and fiber on the other hand (Scheme 1). However, as previously reported,<sup>12</sup> the reaction could also be extended to a copolymerization between a grafted CD unit and another CD molecule, by the intermediate of a new PCA crosslinking agent. To summarize, CD is grafted onto the cellulosic fiber directly and also by the formation of a copolymer issued from the reaction between CD units and PCA.

### Adjustment of the Curing Parameters

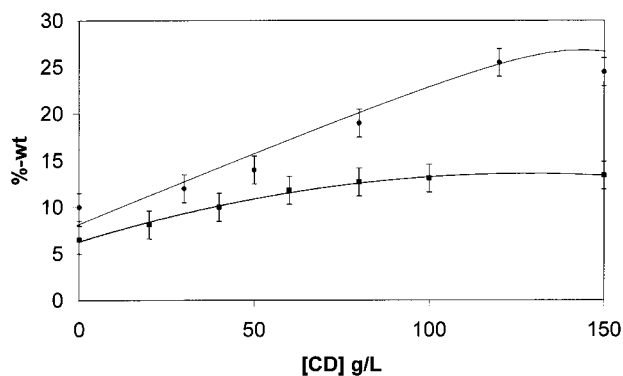
In a preliminary study, time and temperature of curing of the fabrics were also investigated. As shown in Figure 2, the amount of grafted CTR onto the cotton fabric reached a plateau at a temperature  $>155$  °C. On the other hand, the grafting of  $\beta$ -CD could be detected only at temperatures  $>160$  °C (dashed curve). These results show that the esterification reaction between CTR and cellulose occurred at a lower temperature than that with CD. As a consequence, we chose a temperature of 195 °C and a curing time of 5 min as typical parameters for most of the following experiments.



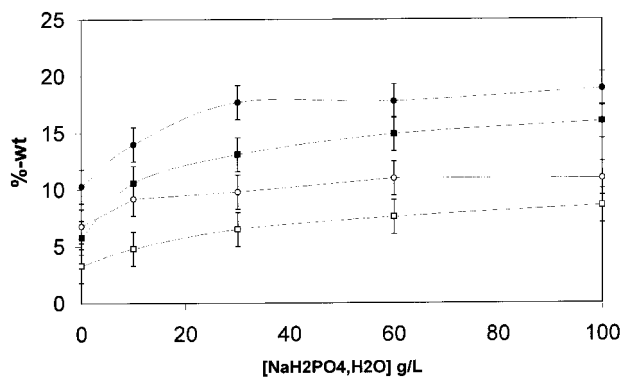
**Figure 2** Influence of the temperature of curing (curing time = 5 min) on the grafting yield, in the presence of (open symbols) CTR alone and (solid symbols) CTR +  $\beta$ -CD ( $[\beta$ -CD] = 100 g/L). The dashed curve represents the calculated amount of fixed CD.

#### Influence of the CD Concentration in the Impregnating Bath

In Figure 3, it is observed that the %wt of the cotton samples varied with the  $\beta$ -CD concentration in the impregnation bath. It is also observed that BTCA allowed better grafting yields than CTR. On one hand, this feature can be attributed to the higher degree of functionalization of BTCA (4 carboxyl groups instead of 3). On the other hand, this feature may be attributed to the fact that BTCA forms a five-membered cyclic anhydride intermediate that is more reactive than the six-membered cyclic anhydride formed by CTR, as reported by Welsh et al.<sup>16</sup> and Yang et al.<sup>17</sup> who compared both PCA efficiencies in the durable press finishing process.



**Figure 3** Weight gain of the cotton fabrics treated with variable concentrations of  $\beta$ -CD [ $\blacksquare$ ] = [CTR] = 100 g/L;  $\bullet$ ] = [BTCA] = 100 g/L], with  $[\text{NaH}_2\text{PO}_4, \text{H}_2\text{O}] = 30 \text{ g/L}$ , and curing at 195 °C for 5 min.

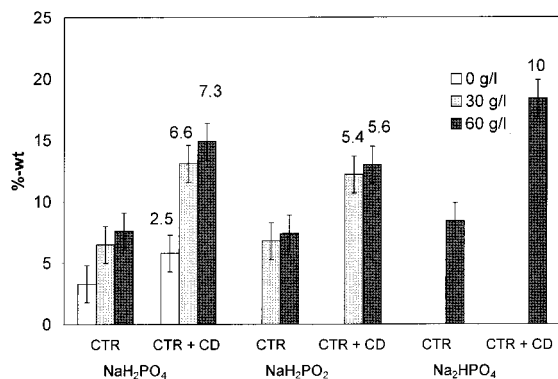


**Figure 4** Weight gain of the cotton fabrics treated with variable concentrations of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  in the presence of BTCA and CTR, with or without  $\beta$ -CD, and with curing at 195 °C for 5 min. Key:  $\blacksquare$ : [CTR] = 100 g/L and  $[\beta$ -CD] = 100 g/L;  $\square$ : [CTR] = 100 g/L;  $\bullet$ : [BTCA] = 100 g/L and  $[\beta$ -CD] = 100 g/L;  $\circ$ : [BTCA] = 100 g/L.

#### Influence of the Concentration and the Nature of the Catalyst

The influence of the concentration of the catalyst ( $\text{NaH}_2\text{PO}_4$ ) on the reaction is presented in Figure 4. Because BTCA and CTR were kept constant at 100 g/L in the impregnation bath, the experiments were conducted in the absence (open symbols) and in the presence (full symbols) of  $\beta$ -CD (100g/L). A plateau was raised for a catalyst concentration  $>30 \text{ g/L}$  when BTCA was used as crosslinking agent, whereas a continuous slight increase could be observed in the range of concentration studied for CTR. In both cases, the necessity of a catalyst is obvious and a concentration of 30 g/L was chosen as the best compromise with regard to the grafting yield.

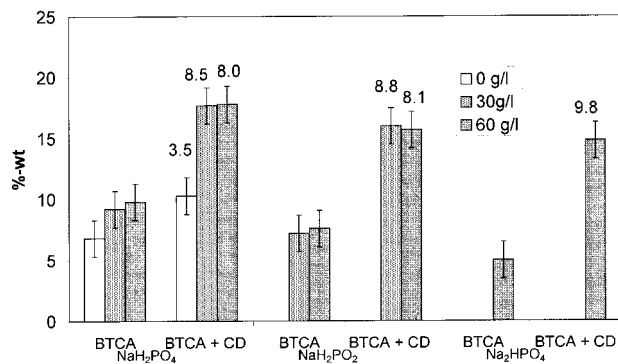
We also compared three phosphorous catalysts previously used in the durable press finishing of cotton by polycarboxylic acids.<sup>17</sup> These catalysts were tested in the presence or absence of  $\beta$ -CD, with CTR, BTCA, and PAA were used as crosslinking agents. The results are shown in Figures 5–7. For the three PCAs studied, it is not possible to depict a common best catalyst considering the grafting yield of  $\beta$ -CD. Three optimal compositions of the impregnating solutions are presented as the following triads: ( $\text{Na}_2\text{HPO}_4$ /CTR/ $\beta$ -CD); ( $\text{NaH}_2\text{PO}_4$ /BTCA/ $\beta$ -CD), and ( $\text{NaH}_2\text{PO}_2$ /PAA/ $\beta$ -CD). In most cases, no sharp difference was observed for experiments carried out with 30 and 60 g/L of catalyst. Figures 7 and 8 show that PAA has generally the best ability to fix  $\beta$ -CD onto the cotton support. This result could be unexpected considering its low yield of



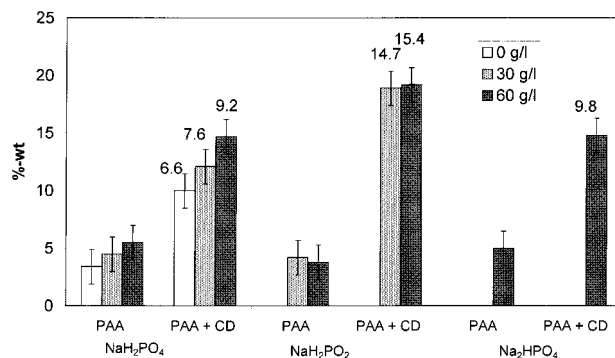
**Figure 5** Weight gain of cotton fabrics treated with CTR (100 g/L), no  $\beta$ -CD or  $[\beta$ -CD] = 100 g/L, and no catalyst or [catalyst] = 30 or 60 g/L. Values over the columns represent the calculated add-on in CD.

esterification with cellulose (in the absence of CD) compared with that of the other two PCAs of this study. We agree with the interpretation proposed by Yang and Wang<sup>18</sup> that the reactivity of this macromolecular PCA is affected by comparison with that of the low molecular weight PCA. On the contrary, as presented in Figure 8, despite its low reactivity towards the support, PAA is a better linking agent to CD than BTCA and CTR. We suppose that PAA polymer chains are grafted to cotton fibers by the intermediate of few ester links. As a consequence, the grafted macromolecular chains contain many remaining free carboxylic acid groups that are available to react with CD. In addition, the presence of  $\beta$ -CD in the impregnating solution probably promotes the grafting of the PCA onto the fibrous support.

When PAA was directly used in its sodium salt form (NaPAA), no grafting occurred (0 %-wt).

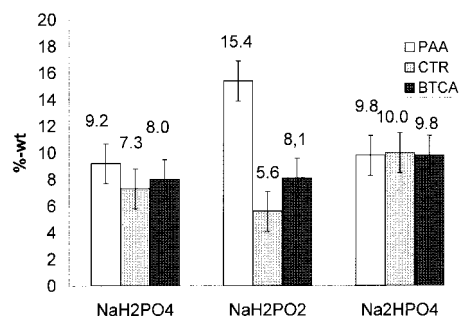


**Figure 6** Weight gain of the cotton fabrics treated with BTCA (100 g/L), no  $\beta$ -CD or  $[\beta$ -CD] = 100 g/L, and no catalyst or [catalyst] = 30 or 60 g/L. Values over the columns represent the calculated add-on in CD.



**Figure 7** Weight gain of the cotton fabrics treated with PAA (100 g/L), no  $\beta$ -CD or  $[\beta$ -CD] = 100 g/L, and no catalyst or [catalyst] = 30 or 60 g/L. Values over the columns represent the calculated add-on in CD.

However, as shown in Table I, the same experiment was more successful (2.8 %-wt) when the pH of the impregnating solution was adjusted from 6.9 (natural pH of the NaPAA solution) to 3.0 by addition of concentrated hydrochloric acid. On the other hand, the combination of the adjustment of the pH to 3.0 and the use of NaH<sub>2</sub>PO<sub>2</sub> as catalyst gave rather good results in the graft reaction of  $\beta$ -CD (12 %-wt). In the last experiment, the reaction yield decreased sharply in the absence of catalyst. We conclude that the reaction is controlled at the same time by the pH of the solution and by the role played by the catalyst. In fact, the low pH value is necessary to impose the acidic form of the carboxylic groups, a condition that is favorable to their dehydration to yield anhydride groups. On the other hand, the presence of the catalyst favors the formation of the cyclic anhy-



**Figure 8** Grafting yield in %-wt of  $\beta$ -CD onto cotton versus the nature of the crosslinking agent (100 g/L) and of the catalyst (60g/L). Values calculated from the difference of weight increase of fabrics treated in the presence (100 g/L) and in absence of  $\beta$ -CD. Values over the columns represent the calculated add-on in CD.

**Table I Study of the Influence of the pH of the Reaction Medium and of the Role of the Catalyst on the Grafting Reaction**

NaPAA (g/L)	$\beta$ -CD (g/L)	$\text{NaH}_2\text{PO}_2 \cdot x\text{H}_2\text{O}$ (g/L)	pH	Weight Gain (%-wt)	CD Add-on
100	—	30	6.9	0.0	—
100	—	30	3.0	2.8	—
100	100	30	3.0	14.8	12.0
100	100	—	3.0	7.3	4.5

drude intermediates and its further reaction with cellulose.<sup>19</sup>

### Generalization of the Process to Other Cyclodextrins

The results shown in Figures 9 and 10 confirm that the functionalization process reported in this paper is also applicable to the other members of the CD family, especially to  $\alpha$ - and  $\gamma$ -CD. The grafting yield of CD onto the cotton fiber is of the same order for  $\alpha$ - and  $\beta$ -CD and slightly superior in the case of  $\gamma$ -CD (Figure 9). From the experiments it is not possible to depict a typical catalyst that would give the best efficiency in the grafting of the three CDs: sodium hydrogen phosphate is better for  $\alpha$ - and  $\beta$ -CD and sodium hypophosphite is better for  $\gamma$ -CD. When comparing the three crosslinking agents, BTCA and PAA appeared to bind to CDs more efficiently than CTR. On the other hand, experiments carried out with RAMEB resulted in lower fabric weight gain than that obtained for the parent  $\beta$ -CD: a maximum

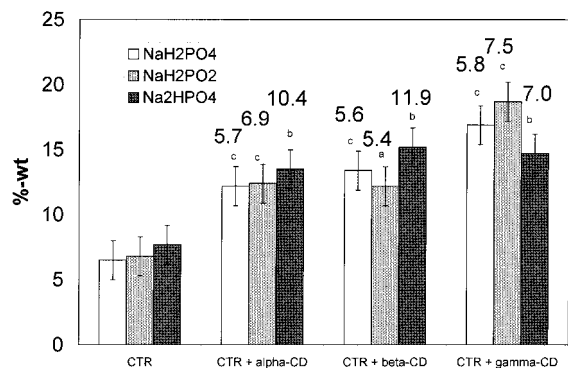
value of only 3%-wt was attained. This difference is probably due the low hydroxyl content of RAMEB that has an influence on the yield of the esterification reaction.

### Characterization by Infrared Spectroscopy

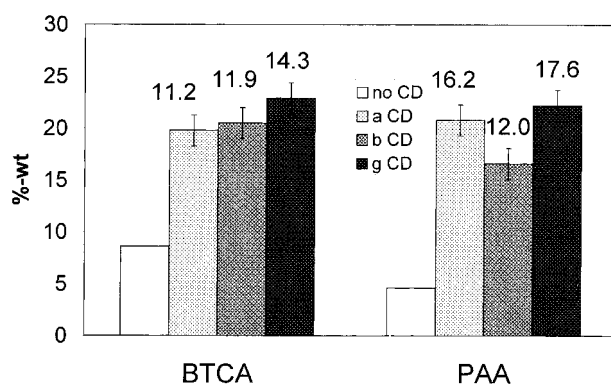
The IR spectra of the control cotton and a cotton treated by  $\beta$ -CD and CTR are shown in Figure 11. The main difference that one can observe is the appearance of a band at  $1730\text{ cm}^{-1}$  that is attributed to both the carbonyl band of the ester formed during the curing process and the carboxyl carbonyl band of the PCA. Because of the similarity of the structure of cotton cellulose and CD, they can hardly be distinguished on the spectrum (spectrum b on Figure 11)

### Extension of the Process to Wool

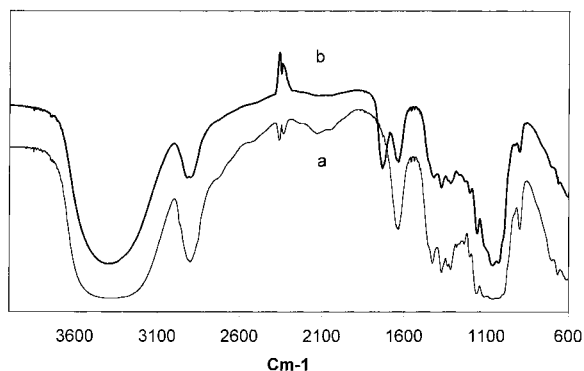
Wool can undergo many types of reaction because of the chemical reactivity of keratin in its fibers. Using the same parameters as described for cotton, we conducted experiments with wool, and the



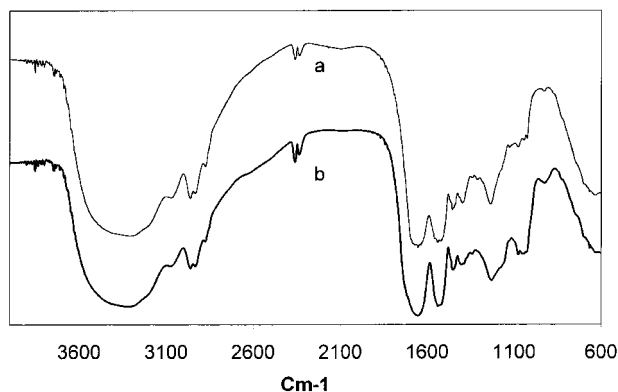
**Figure 9** Weight gain of cotton fabrics treated with CTR (100 g/L) and three different catalysts ( $[\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}] = [\text{NaH}_2\text{PO}_2 \cdot x\text{H}_2\text{O}] = 30\text{ g/L}$ ;  $[\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}] = 60\text{ g/L}$ ) and three different cyclodextrins (a : [CD] = 10 g/L; b : [CD] = 12.5 g/L; c : [CD] = 15 g/L). Values over the columns represent the calculated add-on in CD.



**Figure 10** Weight increase of cotton fabrics treated with [BTCA] or [PAA] = (100 g/L) and three different cyclodextrins ( $[\text{NaH}_2\text{PO}_2 \cdot x\text{H}_2\text{O}] = 30\text{ g/L}$ ;  $[\beta\text{-CD}] = 100\text{ g/L}$ ;  $[\alpha\text{-CD}] = [\gamma\text{-CD}] = 150\text{ g/L}$ ). Values over the columns represent the calculated add-on in CD.

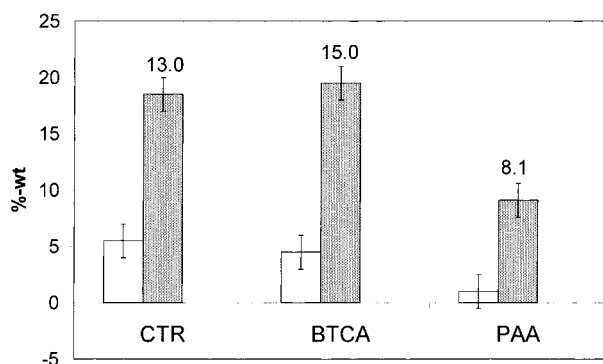


**Figure 11** Infrared spectra of (a) cotton and (b) cotton treated with  $\beta$ -CD and CTR.



**Figure 13** Infrared spectra of (a) wool and (b) wool treated with  $\beta$ -CD and CTR.

results are presented in Figure 12. The three PCAs induced successful graftings of  $\beta$ -CD onto the support. The difference of the %-wt between experiments carried out in the presence and in absence of CD is sharp. This result indicates that a great amount of CD was grafted, especially when CTR and BTCA were used. The respective efficiency of the three crosslinking agents is different from that observed for cotton finishing. PAA gave a surprising result as it was almost unreacted when present alone in the impregnation bath, whereas a noticeable weight increase of the fabric was measured in the presence of CD. This result can be compared with what has been previously observed with cotton. FTIR spectroscopy confirmed the grafting of CD onto the wool fibers by the appearance of the typical absorption band in the  $1000\text{--}1100\text{-cm}^{-1}$  region (Figure 13).



**Figure 12** Weight gain of wool fabrics treated with three PCA, without and with  $\beta$ -CD.  $[\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}] = 60 \text{ g/L}$ .  $[\beta\text{-CD}] = 150 \text{ g/L}$  for CTR and  $[\gamma\text{-CD}] = 100 \text{ g/L}$  for BTCA and PAA. Values over the columns represent the calculated add-on in CD.

## CONCLUSIONS

We report the details of a study of a new method for the grafting of CDs onto cotton or wool. The novelty of this method is more the chemical approach (the use of polycarboxylic acids as grafting intermediates) of the reaction than the process used (pad-dry-cure). Its advantages, compared with the other methods previously proposed in the literature, are that all the reactants involved are nontoxic, environmentally friendly, and have a low cost, and all native CDs and their derivatives can be fixed, as long as they carry enough remaining OH groups. Therefore, this method offers some technical, economic, and ecological interest. In coming reports, the extension of the technique to other fibers will be detailed and the complex-forming ability of the grafted CDs towards some organic substances will be investigated.

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