

Grafting of Cotton with β -Cyclodextrin via Poly(carboxylic acid)

B. Voncina, A. Majcen Le Marechal

Textile Department, Faculty of Mechanical Engineering, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia

Received 9 April 2004; accepted 10 October 2004

DOI 10.1002/app.21442

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Cyclodextrins are cyclic oligosaccharides. Cyclodextrin molecules can form inclusion complexes with a large number of organic molecules. The properties of cyclodextrins enable them to be used in a variety of different textile applications. Cyclodextrins can act as auxiliaries in washing and dyeing processes, and they can also be fixed onto different fiber surfaces. Because of the complexing abilities of cyclodextrins, textiles with new functional properties can be prepared. Poly(carboxylic acid)s such as 1,2,3,4-bu-

tane tetracarboxylic acid (BTCA) are well-known non-formaldehyde crosslinking reagents. BTCA has four carboxylic acid groups, which can react with hydroxyl groups of cellulose and form stable ester bonds. We crosslinked β -cyclodextrin molecules on hydroxyl groups of cellulose via BTCA. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1323–1328, 2005

Key words: FTIR; fibers; host–guest systems

INTRODUCTION

Cyclodextrins (CDs), which are cyclic oligosaccharides, are macrocyclic compounds built from glucopyranose units linked by α -(1,4)-glycosidic bonds.^{1,2} CDs can be obtained through the enzymatic degradation of starch. In this process, compounds with 6–12 glucopyranose units per ring are produced. According to the enzyme and the way in which the reaction is controlled, the main product is α -CD, β -CD, or γ -CD (6, 7, or 8 glucopyranose units, respectively).

They are circular and conical; the height is approximately 800 pm. The inner diameter of the cavity varies from 500 to 800 pm (Fig. 1).^{2,3}

Cramer and coworkers^{4–7} systematically studied the formation of CD guest complexes. β -CD is commercially most interesting because of its simple production, availability, cavity diameter, and price. It is most widely used and counts for at least 95% of all produced and consumed CDs.⁸ The inner diameter of the β -CD cavity varies from 600 to 680 pm^{9,10} and can accommodate aromatic compounds such as volatile molecules and drugs.

The new concept for the modification of textile substrates is based on the permanent fixation of supramolecular compounds, such as CDs, on the material surface, which impart new functionality to the fabric.¹¹ Textile substrates treated in this way will be important for medical and hygienic textiles and garment and

home textiles.¹² From the structure of β -CD, it is evident that it cannot form a direct covalent bond with textile fibers.

Poly(carboxylic acid)s such as 1,2,3,4-butane tetracarboxylic acid (BTCA) are well known non-formaldehyde crosslinking reagents. BTCA has four carboxylic acid groups, which can react with hydroxyl groups of cellulose and form stable ester bonds.¹³ Rowland et al.¹⁴ studied in detail the esterification reactions of poly(carboxylic acid)s with cotton cellulose. This and subsequent work indicated that a high level of cellulose crosslinking could be obtained with a poly(carboxylic acid) with three or more carboxyl groups per molecule.^{14–19} Esterification can occur with heat alone or can be accelerated by the presence of salts of weak acids, such as sodium hypophosphite (SHPI). Welch²⁰ established that the physical properties of cotton fabrics treated with BTCA were comparable to those of cotton treated with the most effective *N*-methylol reagents, such as *N,N'*-dimethyloldihydroxyethylene urea.

In our research, we fixed β -CD onto cotton cellulose via grafting or crosslinking with BTCA, as shown in Figure 2.

EXPERIMENTAL

Cotton (100%) that was desized, scoured, bleached, and mercerized on continuous production equipment, with a mass of 140 g/m², was used.

Fabric treatment

The mercerized cotton was immersed in treatment baths with different concentrations of β -CD and

Correspondence to: B. Voncina (bojana.voncina@uni-mb.si).

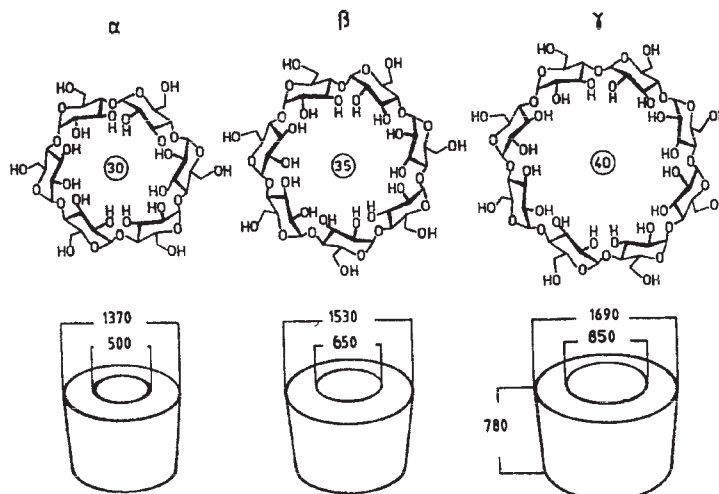


Figure 1 Structures and dimensions of CDs. From *Supramolecular Chemistry: An Introduction*, by Fritz Vögtle, 1991, New York: Wiley. Copyright 1991 by John Wiley & Sons, Inc. Reprinted with permission.

BTCA; for the reduction of the curing temperature, the catalyst SHPI was used. The wet pickup was 150%, and the cloth was predried at 110°C for 10 min. The fixation was carried out at 170°C for 3 min when the catalyst SHPI was used and at 200°C for 3 min when finishing was carried out without the addition of the catalyst. The concentrations of β -CD, BTCA, and SHPI in the finishing baths and the curing temperatures are shown in Table I. The pH of every finishing bath was 2.7. The treated textile material was rinsed in cold water and washed for 30 min at 60°C with the addition of a nonionic surfactant.

Qualitative determination of β -CD molecules on the textile substrate

β -CD molecules on the textile substrate were determined with phenol red and phenolphthalein. Phenol

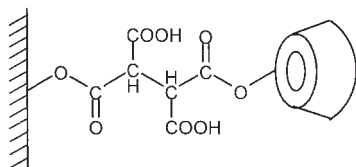


Figure 2 Grafting β -CD onto hydroxyl groups of cellulose via BTCA.

TABLE I
Concentrations of β -CD, BTCA, and SHPI in the Finishing Baths and Curing Temperatures

Concentration of β -CD in the finished bath (g/L)	Concentration of BTCA in the finished bath (g/L)	Concentration of SHPI in the finished bath (g/L)	Curing temperature (°C)
30	6	6	170
100	6	6	170
30	6	—	200

red forms a yellow complex with β -CD, so phenol red changed color from red to yellow when β -CD was present on the textile substrate (shown later in Figs. 4 and 6). Figure 5 and 7 (shown later) present the change in the color of phenolphthalein from carmine red for the untreated textile substrate to colorless for the BTCA/ β -CD-treated textile materials.

Determination of β -CD grafting onto hydroxyl groups of cellulose via BTCA

When cotton fabrics were treated with BTCA and β -CD, esterification between BTCA, β -CD, and hydroxyl groups of cellulose occurred at elevated temperatures. After the unreacted BTCA was washed, the carbonyls retained in the fabrics existed in three forms: esters, carboxylic acids, and carboxylate anions.^{21–24} In IR spectra, the band due to an ester carbonyl group appeared around 1720 cm^{-1} , and the band due to a carboxylic acid carbonyl group appeared in the same region. In the BTCA/ β -CD-finished cotton, the band for the ester group could not be resolved without further fabric treatment. The carboxylic acid group could be converted into carboxylate anions by the posttreatment of fabrics in an alkaline solution (Fig. 3). Therefore, the posttreatment of BTCA- and β -CD-finished fabrics with alkaline solutions separated the es-

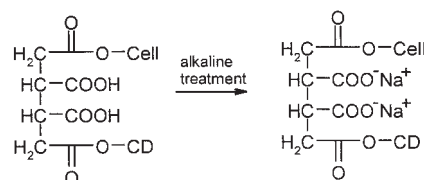


Figure 3 Conversion of carboxylic acid groups into carboxylate anions.

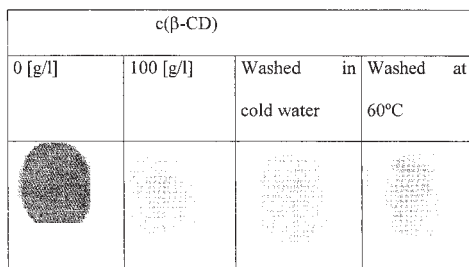


Figure 4 Change in the phenol red color from red to yellow for fabrics treated in solutions containing 100 g/L β -CD, thermofixed, rinsed in cold water, and washed at 60°C for 30 min.

ter carbonyl band from the acid carbonyl band. In IR spectra of alkaline-posttreated BTCA/ β -CD-finished fabrics, a band at 1580 cm^{-1} appeared, and the intensity of the 1720- cm^{-1} band decreased. IR spectroscopy was carried out with a PerkinElmer Fourier transform infrared (FTIR) spectrophotometer with a Golden Gate attenuated total reflection (ATR) attachment with a diamante crystal.

Evidence of grafting from weight-gain measurements of the finished cotton fabrics

The weight gain of the finished fabrics was measured (for samples treated in 30 g/L β -CD and 100 g/ β -CD with the addition of 6 g/L BTCA and 6 g/L SHPI) to yield the efficiency of the reaction according to standard test method DIN 53814. The samples were dried for 4 h at 105°C and weighed before and after the finishing. All experiments were carried out in triplicate; the means of the weight percentages were calculated.

Wrinkle recovery angle (WRA)

The standard test method for the wrinkle recovery of woven textile fabrics with a vertical strip apparatus was used to measure the conditioned WRA (ISO 9867).

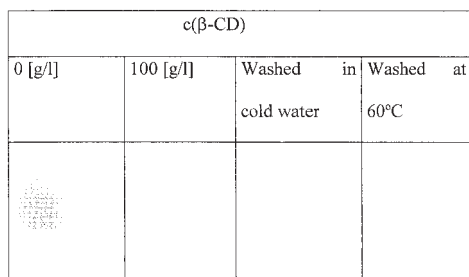


Figure 5 Change in the phenolphthalein color from carmine red to colorless for fabrics treated in solutions containing 100 g/L β -CD, thermofixed, rinsed in cold water, and washed at 60°C for 30 min.

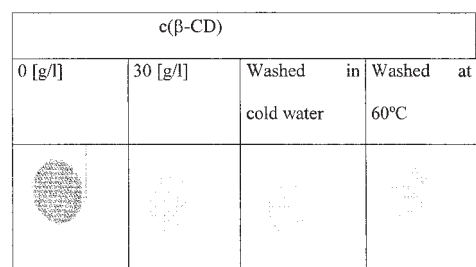


Figure 6 Change in the phenol red color from red to yellow for fabrics treated in solutions containing 30 g/L β -CD and 6 g/L BTCA, thermofixed, rinsed in cold water, and washed at 60°C for 30 min.

RESULTS AND DISCUSSION

From the color reactions²⁵ of β -CD with phenol red (Fig. 4) and phenolphthalein (Fig. 5), we concluded that β -CD grafted onto hydroxyl groups of cellulose via BTCA remained on the material after rinsing in cold water and after washing for 30 min at 60°C. The best results were obtained when the material was treated in a bath containing 100 g/L β -CD, 6 g/L BTCA, and 6 g/L SHPI. The optimum curing temperature in the presence of phosphorous catalyst SHPI was 170°C. If the curing was carried out without the catalyst, the curing temperature had to be higher. Figures 6 and 7 present the color reactions of β -CD molecules bonded onto cellulose substrates via BTCA (curing was carried out at 200°C without the addition of SHPI). Figure 7 shows that the carmine red color appeared for the sample treated in a finishing bath containing 30 g/L β -CD and 6 g/L BTCA, thermofixed at 200°C without the addition of SHPI, and washed at 60°C for 30 min. The intensity of the colored stain was lower than the intensity of carmine red of an untreated cotton sample, and this proved that washing at a higher temperature caused some ester bonds to hydrolyze.

Figure 8 shows two ATR-FTIR spectra of BTCA/ β -CD-finished cotton fabrics: the spectrum of a BTCA/

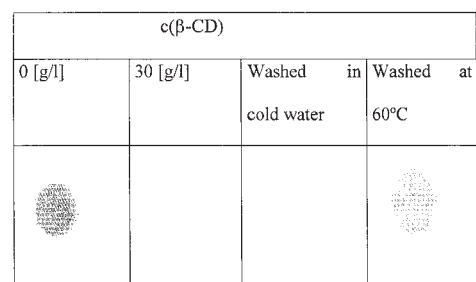


Figure 7 Change in the phenolphthalein color from carmine red (for untreated cotton fabrics) to colorless for fabrics treated in solutions containing 30 g/L β -CD and 6 g/L BTCA, thermofixed, rinsed in cold water, and washed at 60°C for 30 min.

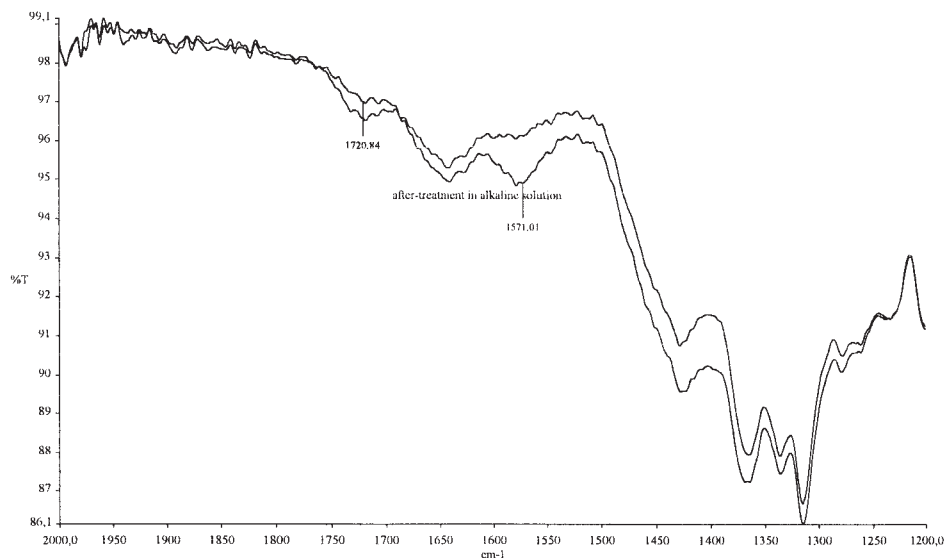


Figure 8 ATR-FTIR spectra of BTCA/ β -CD-finished cotton fabrics.

β -CD-finished textile material and the spectrum of cotton fabric BTCA/ β -CD-finished and alkaline-post-treated. The posttreatment of BTCA/ β -CD-finished cotton fabrics in an alkaline solution separated the ester carbonyl band from the carboxylic acid band; the intensity of the 1720-cm^{-1} band decreased, and a new band at 1567 cm^{-1} for the carboxylate anions appeared.

For better presentation, the differential ATR-FTIR spectrum of BTCA/ β -CD-treated and alkaline-solution-posttreated cotton fabrics is presented (the cotton spectrum was subtracted). Figure 9 presents the differential spectrum of BTCA/ β -CD-finished and alkaline-solution-posttreated cotton fabrics. The band at 1720 cm^{-1} is present in the spectrum, and this indicates that there were ester links between BTCA and

hydroxyl groups of cellulose, hydroxyl groups of β -CD, or both. Figure 10 shows the differential ATR-FTIR spectrum of cotton fibers BTCA/ β -CD-finished, washed at 60°C , and alkaline-solution-posttreated. After the washing, some of the ester links were hydrolyzed; the intensity of the ester band at 1720 cm^{-1} was lower than that of the unwashed, BTCA/ β -CD-treated, alkaline-solution-posttreated sample.

ATR-FTIR spectroscopy of nanoencapsulated cotton fabrics showed that after washing at 60°C for 30 min, the band at 1720 cm^{-1} was still present. The results from IR spectroscopy were confirmed with the results obtained from color reactions with phenol red and phenolphthalein.

Figure 11 presents the differential ATR-FTIR spectrum of cotton fabrics BTCA/ β -CD-treated (curing



Figure 9 Differential ATR-FTIR spectrum of BTCA/ β -CD-finished cotton (100 g/L β -CD, 6 g/L BTCA, and 6 g/L SHPI in the finishing bath) rinsed in cold water after an alkaline solution posttreatment (the spectrum of cotton was subtracted).



Figure 10 Differential ATR-FTIR spectrum of BTCA/ β -CD-finished cotton (100 g/L β -CD, 6 g/L BTCA, and 6 g/L SHPI in the finishing bath) rinsed in cold water and washed at 60°C for 30 min after an alkaline solution posttreatment (the spectrum of cotton was subtracted).

was carried out at 200°C without the addition of SHPI), washed at 60°C, and alkaline-posttreated. The band at 1720 cm^{-1} indicates that esterification without the addition of the catalyst SHPI occurred at 200°C, although the colored reaction of β -CD with phenolphthalein (Fig. 7) showed that during the washing at 60°C, some BTCA was hydrolyzed.

During the grafting of β -CD via BTCA onto hydroxyl groups of cellulose, an increase in the weight occurred. According to the grafting reaction (Fig. 3), the molar ratio of β -CD to BTCA was 1:1. The weight increase of the cotton fabrics finished with β -CD via BTCA was 2.03% (for the treatment in the finishing bath containing 30 g/L β -CD) or 3.46% (for the treat-

ment in the finishing bath containing 100 g/L β -CD). The molecular weight of β -CD ($M_w = 1135$) was approximately 4.8 times higher than the molecular weight of BTCA ($M_t = 234$), so the actual weight percentage gain of the finished cotton fibers decreased to 1.6 and 2.7%, respectively.

When hydroxyl groups of cellulose were crosslinked with BTCA (regardless of the catalyst presence), significant improvements in WRA were obtained. On the other hand, when BTCA was coapplied to cotton fabrics with β -CD, the WRA values were lower than those of untreated cotton fibers. This could be an indication that only grafting, not crosslinking, of β -CD onto hydroxyl groups via BTCA occurred.



Figure 11 Differential ATR-FTIR spectrum of BTCA/ β -CD-treated cotton (curing was carried out at 200°C without the addition of SHPI at 200°C) rinsed in cold water and washed at 60°C for 30 min after an alkaline solution posttreatment (the spectrum of cotton was subtracted).

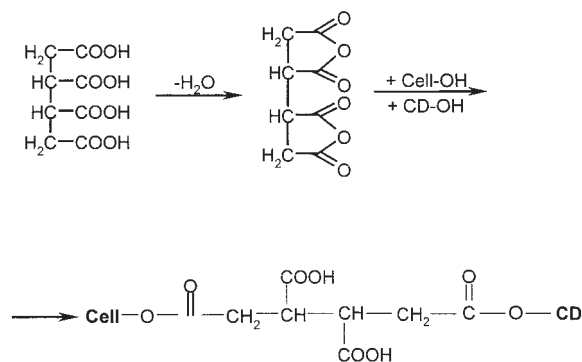


Figure 12 Proposed grafting reaction of β -CD onto hydroxyl groups of cellulose via BTCA.

Much work has been done to elucidate the crosslinking mechanism of BTCA onto hydroxyl groups of cellulose. Welch²⁰ suggested that the crosslinking of cellulose with poly(carboxylic acid)s initially involves the formation of an intermediate cyclic anhydride, which then reacts further with cellulose hydroxyl groups to form ester bonds. According to the second mechanism,²⁶ a linear mixed anhydride was formed at an elevated temperature in the presence of the catalyst SHPI; when no catalyst was used in the curing procedure, a cyclic anhydride was formed. The mechanisms of crosslinking depended on the catalysts.

Poly(carboxylic acid)s with three or four carboxylic acid groups, such as BTCA, can form an anhydride more than once. When cellulose fibers were cotreated with BTCA and β -CD, at elevated temperatures BTCA could act as a grafting intermediate. According to previous research on the crosslinking of hydroxyl groups of cellulose with BTCA^{21–24,26} and our current research, regardless of the actual reaction mechanism (the formation of linear mixed or cyclic anhydrides), we can propose a grafting reaction of β -CD onto hydroxyl groups of cellulose via BTCA (see Fig. 12).

CONCLUSIONS

From color reactions with phenol red and phenolphthalein, ATR-FTIR spectroscopy, and WRA mea-

surements, we can conclude that the grafting of β -CD onto cellulose fibers can occur at elevated temperatures. Thus, a nanoencapsulated textile material can be obtained that is resistant to washing. Such BTCA/ β -CD-modified textile materials can form complexes with sweat components or can release included volatile molecules or pharmaceutical compounds over a long period of time.

References

- Freudenberg, K.; Cramer, F. *Z Naturforsch B: Chem Sci* 1948, 3, 464.
- Vögtle, F. *Supramolecular Chemistry: An Introduction*; Wiley: New York, 1991; p 135.
- Weber, E. *Top Curr Chem* 1987, 140, 1.
- Cramer, F. *Einschlussverbindungen*; Springer: Heidelberg, 1954.
- Cramer, F.; Hellter, H. *Naturwissenschaften* 1967, 54, 626.
- Cramer, F.; Henglein, F. M. *Chem Ber* 1957, 92, 2561.
- Seanger, W. *Angew Chem Int Ed Engl* 1980, 19, 344.
- Szejtli, J. *Med Res Rev* 1994, 14, 353.
- Szejtli, J.; Osa, T. *Comprehensive Supramolecular Chemistry*; Elsevier: Oxford, 1996; Vol. 3.
- Jozwiakowski, M.; Connors, K. *Carbohydr Res* 1985, 143, 1067.
- Knittel, D.; Schollmeyer, E. *J Text Inst* 2000, 3, 151.
- Buschmann, H.-J.; Knittel, D.; Schollmeyer, E. *Ger. Pat. DP 40 35 378.8* (1990).
- Gagliardi, D. D.; Shippee, F. B. *Am Dye Rep* 1963, 15, 74.
- Rowland, S. P.; Welch, C. M.; Brannan, M. A. F.; Gallagher, D. M. *Text Res J* 1967, 37, 933.
- Kottes Andrews, B. A.; Welch, C. M.; Trask-Morrel, B. J. *Am Dye Rep* 1989, 78, 15.
- Welch, M. C.; Kottes Andrews, B. A. *Text Chem Colorist* 1989, 21, 13.
- Rowland, S. P. *Text Res J* 1968, 38, 643.
- Welch, C. M. *Text Chem Colorist* 1990, 22(5), 13.
- Brown, R. O. *Book of Papers, American Association of Textile Chemists and Colorists International Conference and Exhibition, Charlotte, VA, 1991*.
- Welch, C. M. *Text Res J* 1988, 58, 480.
- Lewis, D. M.; Voncina, B. *J Appl Polym Sci* 1997, 66, 1465.
- Lewis, D. M.; Voncina, B. *J Appl Polym Sci* 1997, 66, 171.
- Yang, C. Q. *Text Res J* 1991, 61, 433.
- Martel, B.; Weltrowski, M.; Ruffin, D.; Morcellet, M. *J Appl Polym Sci* 2002, 83, 1449.
- Beermann, K.; Buschmann, H.-J.; Knittel, D.; Schollmeyer, E. *Textilveredlung* 2002, 1, 17.
- Gillingham, E. L.; Lewis, D. M.; Voncina, B. *Text Res J* 1999, 69, 949.