Surface Modification of PET Fibers with the Use of β-Cyclodextrin

Bojana Voncina,[1] Vera Vivod,[1] Wen-Tung Chen[2]

[1]*Department of Textile Materials and Design, University of Maribor, Maribor, Slovenia*
[2]*Taiwan Textile Research Institute, Tucheng City, Taipei County, Taiwan*

Received 20 September 2007; accepted 14 February 2009
DOI 10.1002/app.30400
Published online 27 May 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The purpose of our research was to prepare nanoencapsulated PET textile materials, which would be used as odor carriers (underwear and bed sheets with aromatherapy activities) or would act as malodorous absorbers (absorption of cigarette smell). We grafted β-cyclodextrin onto PET textile materials by using a polyfunctional reagent 1,2,3,4-butanetetracarboxylic acid. To reduce the curing temperature of the reaction, catalysts such as sodium hypophosphite and cyanamide were used. We prepared nanoencapsulated polyester textile materials with increased adsorption capacity and with delayed release of volatile or active compounds. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3891–3895, 2009

Key words: supramolecular structures; β-cyclodextrin; crosslinking; polyester; infrared spectroscopy

INTRODUCTION

One of the new concepts for the modification of textile substrates is based on the permanent fixation of supramolecular compounds, such as β-cyclodextrin (β-CD) on the material's surface and, thus, imparts new functionality to the fabric.[1] Cyclodextrins (CDs) are cyclic oligosaccharides. They are macrocyclic compounds built from glucopyranose units linked by α-(1,4)-glycosidic bonds. CDs can be obtained by the enzymatic degradation of starch. During this process, compounds with 6 to 12 glucopyranose units per ring are produced. Depending on the enzyme and the way the reaction is controlled, the main product is α, β, or γ-cyclodextrin (6, 7, and 8 glucopyranose units, respectively). They are of circular and conical conformation, where the height is approximately 800 pm. The inner diameter of the cavity varies from 500 to 800 pm.[2–4] Commercially, the most interesting compound is β-CD because of its simple production, availability, cavity diameter, and price. It is the most widely used CD and presents at least 95% of all produced and consumed CDs.

CDs are able to form host–guest complexes with various hydrophobic molecules. Textile substrates treated with β-CD can be important for medical and hygienic textiles. The ability of complexing fragrances can also be used for garments in cosmetotextile and home textiles.[5] From the structure of β-CD (Fig. 1), it is evident that it is nonreactive; several binders and polyfunctional reagents have been used to link β-CD on textile substrates, mainly on cotton or viscose fibers.[6–9]

Polycarboxylic acids such as 1,2,3,4-butanetetracarboxlic acid (BTCA) are well-known nonformaldehyde crosslinking reagents for the durable press finishing of cellulose fibers. BTCA contains four carboxylic acid groups that can react with various hydroxyl groups and form stable ester bonds. Esterification of hydroxyl groups can occur with heat alone, or it can be accelerated by the presence of salts of weak acids, such as sodium hypophosphite (SHPI). With the use of SHPI, the curing temperature can be reduced from 200°C to 160°C.[10–16] A temperature of 160°C is still too high for the treatment of PET; the handle of the material reduces significantly and some yellowing occurs.

It is known from the literature[17,18] that the presence of cyanamide (CA) significantly reduces the temperature of the esterification of cellulose when BTCA is used. In our previous research,[9] we linked β-CD molecules onto cotton cellulose via grafting with BTCA and observed the establishment of permanent links between hydroxyl groups of β-CD and hydroxyl groups of cellulose. In our current research, we studied the efficiency of β-CD anchoring onto PET textile material by the use of polyfunctional reagent BTCA in the presence of SHPI and CA as catalysts. The efficiency of β-CD bonding onto

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

Contract grant sponsor: Taiwan Textile Research Institute, Taipei, Taiwan.

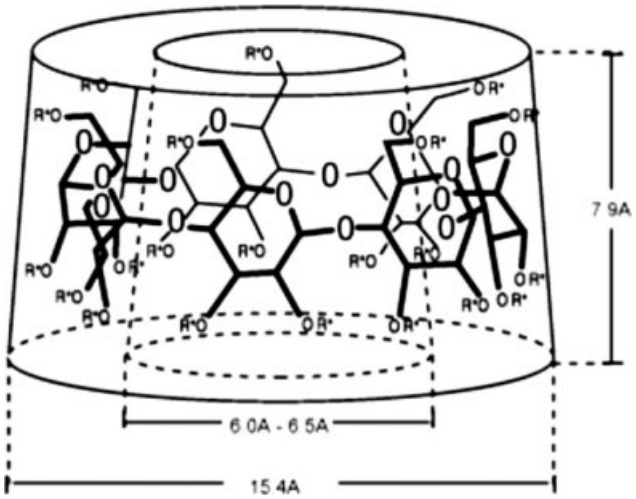

Figure 1 Structure of β-CD.

textile materials was measured with a gravimetrical method. It is well known from the literature that polycarboxylic acids form anhydrides at an increased temperature.[17,19] When anhydrides are formed, they rapidly react with hydroxyl groups and form ester bonds. Here, anhydride formation of BTCA at increased temperatures in the presence of β-CD and CA as a catalyst was studied with the use of attenuated total reflection-Fourier transform infrared (ATR FTIR) spectroscopy.

EXPERIMENTAL

Chemicals

All chemicals used in this work were analytically graded, supplied by Sigma-Aldrich (St. Louis, MO); 100% PET fabric, plain weave, fabric weight of 70.20 g/m^2 was provided by Taiwan Textile Research Institute (Taipei, Taiwan).

Fabric treatment

The PET textile materials were immersed in the treating baths containing β-CD and BTCA. To reduce the curing temperature, the catalyst SHPI or CA was used (concentrations of reagents are shown in Table I). The wet pick up was 100%; all the impregnated cloths were predried at 110°C for 10 min. Fixation was carried out at:

- 160–170°C for 10 min when SHPI as a catalyst was used,
- 100–130°C for 10 min when CA as a catalyst was used.

pH values for all finishing baths were 2.7. The treated and cured textile materials were rinsed in cold water and dried.

Washing

The washings of all three types of textile materials were preceded at 40°C by the use of the standard test method (ISO 105-C01:1987-E).

Evidence of grafting using measurements of the finished fabrics' weight gain

The weight gain of the finished fabrics was measured (DIN 53814) to yield the efficiency of the treatment. The samples were dried for 4 h at 105°C and weighed before and after finishing and rinsing. Five replicates were carried out for each set of experiments.

ATR-FTIR spectroscopy

IR spectroscopy was performed using a Perkin-Elmer FTIR spectrophotometer with a Golden Gate ATR attachment with a diamante crystal. An anhydride formation of BTCA at increased temperature and further reaction with β-CD in the presence of CA as a catalyst was studied with the use of ATR FTIR spectroscopy. The catalyst CA, the crosslinking reagent BTCA, and β-CD were mixed into powder form and heated at increased temperatures. ATR FTIR spectroscopy of such mixtures was conducted.

Adsorption of textile using ammonia gas

The adsorption of ammonia gas onto treated and untreated PET textile materials was measured with the use of the Japan standard test method (JIS K0804).

Odor intensity measurements

To quantify the odor-releasing behavior of β-CD-treated PES fabrics, we organized a sensory panel of nine people to whom the odor was presented under controlled conditions. To study the postponed release of the volatile compounds from the β-CD-treated textile substrate, the following was performed: β-CD/BTCA/CA-treated PET textile substrate was sprayed with perfume and dried; the intensity of the perfume from the untreated PET

TABLE I
Concentrations of β-CD, BTCA, and Catalysts (SHPI, CA) in the Finishing Baths

Conc. of β-CD (%)	Conc. of BTCA (%)	Conc. of SHPI (%)	Conc. of CA (%)
8	6		
8	6	3	
8	6		5[a]

[a] 1% ADHF was added.

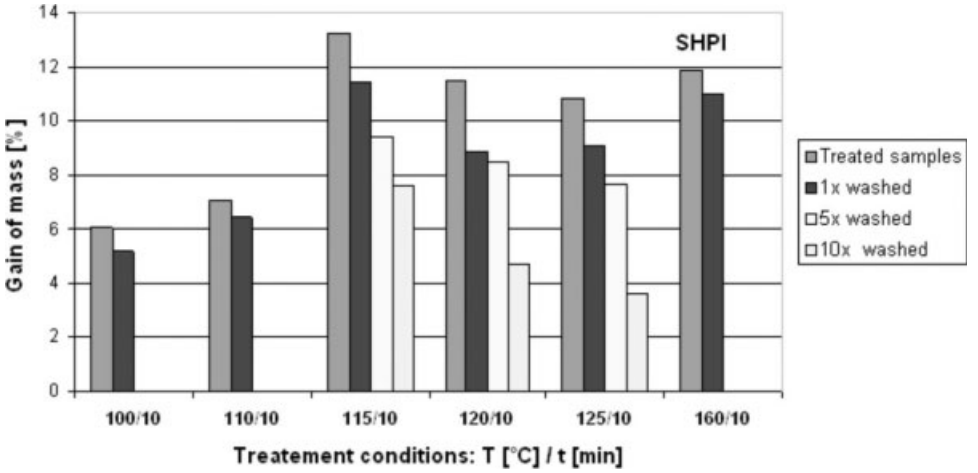

Figure 2 Samples 100/10, 110/10, 115/10, 120/10, and 125/10 are PET samples treated with β-CD, BTCA, CA at 100, 110, 115, 120, and 125°C, respectively; sample 160/10 was treated with β-CD, BTCA, and SHPI at 160°C.

fabric sprayed with perfume was also monitored for comparison purposes. Both treatments were performed in triplicate. The size of the clothes was 10 cm × 10 cm. All perfume-treated textile samples were stored separately in dark places. Samples were stored in open conditions so that the perfume was able to evaporate constantly. The odor release was measured once per week. The smell intensity was evaluated from 0 to 4, with 0 indicating no smell and 4 indicating very intensive smell.

RESULTS AND DISCUSSION

Weight gain

The diagram in Figure 2 presents the gain on mass for PET fibers treated with β-CD, BTCA, CA (concentrations of β-CD, BTCA, and catalysts are presented in Table I) at 100–125°C for 10 min after rinsing in cold water and after washing 1, 5, and 10 times. The weight gain for PET fibers treated with β-CD, BTCA, SHPI at 160°C for 10 min after rinsing in cold water and after washing is presented for comparison purposes. It is possible to conclude that the treatment of PET with β-CD/BTCA was very successful, even at a temperature as low as 115°C, when CA is used as a catalyst. Even after 10 washings (115/10 sample), the weight gain remained as high as 7.8%.

ATR-FTIR spectroscopy

Ducoroy[20] reported that the reaction between β-CD and polycarboxylic acid yielded a crosslinking polymer that was physically anchored onto the PET fibers. BTCA forms anhydrides at increased temperatures; the presence of various catalysts can reduce the temperature of anhydride formation. Anhydrides display two stretching bands within the carbonyl

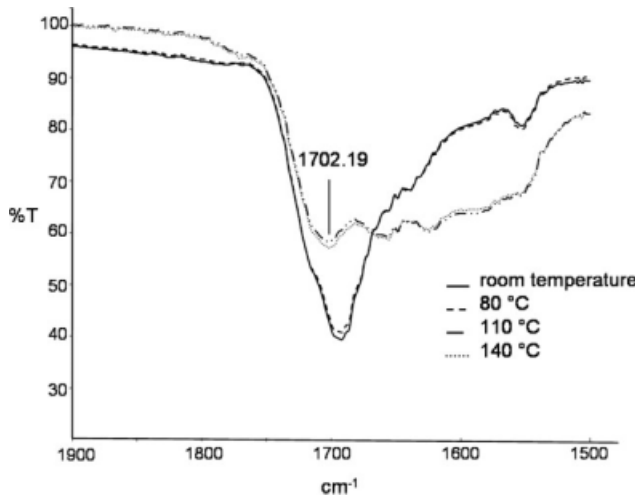

Figure 3 ATR-FTIR spectra of β-CD/BTCA/CA crosslinking system at room and at increased temperatures.

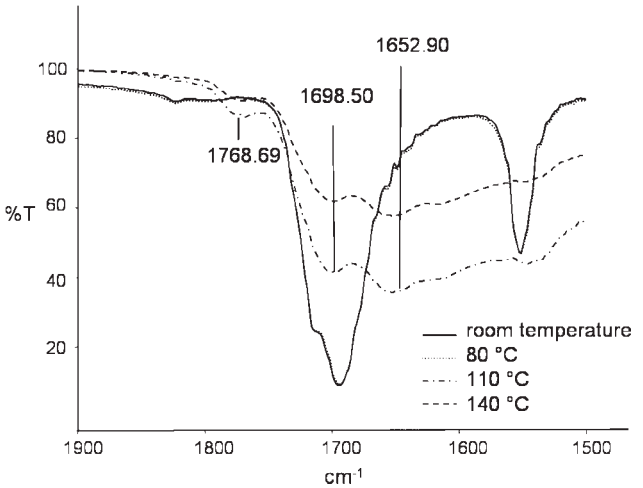

Figure 4 ATR-FTIR spectra of BTCA/CA crosslinking system at room and at elevated temperatures.

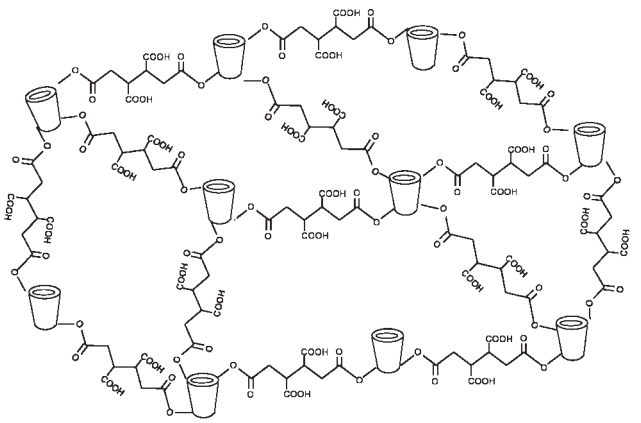

Figure 5 Network of β-CD and BTCA.

region[21]; cyclic anhydrides with a five-member ring show absorbance at around 1865 cm^{-1} for the asymmetrical and at around 1782 cm^{-1} for the symmetrical carbonyl stretching mode. O=C—O—C=O stretching vibrations appear near 1299–1176 cm^{-1} and 952–909 cm^{-1}.

ATR FTIR spectroscopy of the β-CD/BTCA/CA system in powder form was performed (Fig. 3) and also of BTCA/CA without the addition of β-CD (Fig. 4). In the spectra of β-CD/BTCA/CA mixture at room temperature and at 80°C, it is possible to see the presence of one double peak in the 1696–1720 cm^{-1} region; this peak presents the carbonyl vibration of BTCA carboxylic acid groups. At greater temperatures (above 110°C), this double peak decreased in its intensity because carboxylic acid groups form esters with hydroxyl groups of β-CD. The formation of anhydride can not be seen clearly (there are some indications of a peak appearance at 1772 cm^{-1} when the temperature of crosslinking was increased to 140°C) because the anhydride, once formed, reacts rapidly with hydroxyl groups if present.

Figure 4 presents IR spectra of BTCA/CA mixture (β-CD is omitted) at room and increased temperatures. The peak for the anhydride appears at 1768 cm^{-1} when the BTCA/CA mixture is heated above 100°C, whereas the same time the carbonyl band intensity of carboxylic acid group decreases. IR data indicate that the BTCA/CA crosslinking system forms esters with hydroxyl groups of β-CD at 100–110°C.

Gref et al.[22] presented a new supramolecular nanoassembly formed between the hydrophobic alkyl chains and β-CD. By using IR spectroscopy, we derived that BTCA molecules react via anhydride formation with hydroxyl groups of β-CD and form assembly, which can be physically attached to the PET fiber's surface at the increased temperature. The proposed assembly is schematically presented in Figure 5.

TABLE II
Decrease of Ammonium Gas Concentration Attributable to the Adsorption

	β-CD/BTCA/CA at 115°C/10 min	Untreated PES
Initial concentration (ammonia)	125 ppm	125 ppm
1 h concentration (ammonia)	0 ppm	77 ppm

Adsorption of a textile using ammonia gas

From the ammonia gas adsorption measurements (Table II), it is possible to conclude that the adsorption of ammonium gas increased when PET fabric was treated with β-CD/BTCA/CA at 115°C/10 min, after 1 h of exposure to ammonia gas the concentration of gas in the chamber was zero, compare to the concentration when untreated PET fabric was exposed to the ammonium gas, where the concentration in the chamber was changed from the initial value of 125 to 77 ppm.

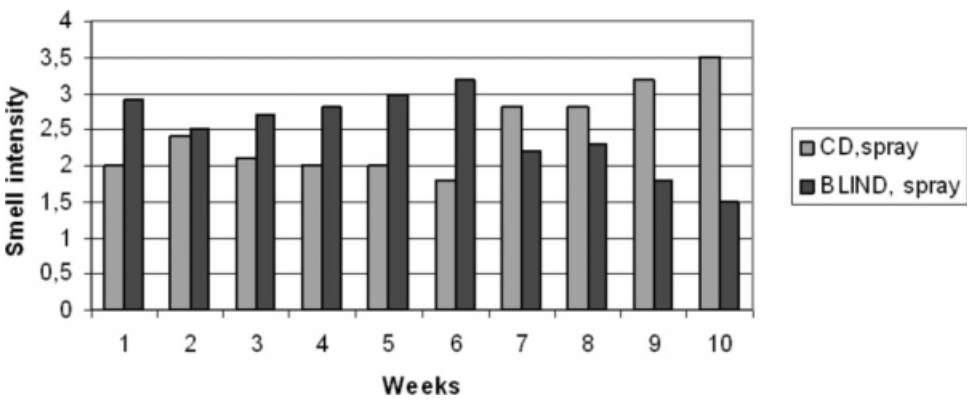

Figure 6 Odor intensity of PET fabrics pretreated with β-CD (light spray) and untreated PET fabrics (dark spray) sprayed with the perfume.

It is possible to conclude that the adsorption effect of a textile treated with β-CD increases significantly compared with the untreated PET fabric.

Odor intensity measurements

Furthermore, we tried to quantify the odor-releasing behavior of β-CD-treated PES fabrics and organized a sensory panel of people to whom the odor was presented under controlled conditions. With β-CD/BTCA/CA-treated PET textile substrate was sprayed with perfume; the intensity of the perfume from the untreated PET sprayed with perfume was also monitored for comparison purposes.

It is possible to see from Figure 6 that the odor release intensity of untreated PET fabrics sprayed with perfume (BLIND, spray) started to decrease after 6 weeks; the odor intensity of perfume sprayed on β-CD-treated fabrics remained constant, but there is a slight indication that the intensity of the perfume began to increase after 6 weeks. We can conclude that, in the case of β-CD-treated PES fabrics, some postponed release of the fragrance occurs.

CONCLUSIONS

In our research we thermofixed PET fibers treated with β-CD and BTCA. Supramolecular assembly was formed between β-CE and BTCA, and such assembly was physically anchored simultaneously onto the textile substrate's surface. To reduce the termofixation temperature, the catalyst cyanamide was used. It is possible to conclude that the treatment of PET with β-CD/BTCA/CA is very successful even at a temperature as low as 115°C. Even after 10 washings, weight gain remained as high as 7.8%. We were able to reduce the curing temperature to 115°C and prepare nanoencapsulated textile materials with increased adsorption capacity and with postponed release of volatile compounds.

Such treated textile materials could be used as a "fragrance-containing textiles" with a delayed release of pleasant odor, e.g., curtains that release a nice smell and at the same time adsorb unpleasant smell from the environment (cigarette smell). When PET fibers treated with β-CD/BTCA/CA and after-treated with perfume are washed, the perfume is washed out; new perfume can be applied on the fabrics by using spraying or dipping.

References

1. Knittel, D.; Schollmeyer, E. J Text Inst Part 2000, 3, 151.
2. Freudenberg, K.; Cramer, F. Z. Naturforcsh Teil B 1948, 3, 464.
3. Vögtle, F. Supramolecular Chemistry: An Introduction; Wiley: New York, 1991; p 135.
4. Weber, E. Top Curr Chem 1987, 140, 1.
5. Buschmann, H.-J.; Knittel, D.; Schollmeyer, E. (Inv Text Material-Cyclodextrin). DP 40,35,378.8 (1990).
6. Martel, B.; Weltrowski, M.; Ruffin, D.; Morcellet, M. J Appl Polym Sci 2002, 83, 1449.
7. Lee, M. H. J Appl Polym Sci 2000, 78, 1986.
8. Lo Nostro, P. J Inclusion Phenom Macromol Chem 2002, 44, 423.
9. Voncina, B.; Majcen Le Marechal, A. J Appl Polym Sci 2005, 96, 1323.
10. Rowland, S. P.; Welch, C. M.; Brannan, F.; Gallagher, D. M. Text Res J 1967, 37, 933.
11. Kottes Andrews, B. A.; Welch, C. M.; Trask-Morrel, B. J. Am Dyes Rep 1989, 78, 15.
12. Welch, M. C.; Kottes Andrews, B. A. Text Chem Colorist 1989, 21, 13.
13. Rowland, S. P. Text Res J 1968, 38, 643.
14. Welch, C. M. Text Chem Colorist 1990, 22, 13.
15. Brown, R. O. Presented at the Book of Papers, American Association of Textile. Chemists and Colorists International Conference and Exhibition, Charlotte, NC, 1991.
16. Welch, C. M. Text Res J 1988, 58, 480.
17. Gillingham, E. L.; Lewis, D. M.; Voncina, B. Text Res J 1999, 69, 949.
18. Rigout, L. A. M.; Lewis, D. M. Appl Spectrosc 2006, 60, 12.
19. Yang, C. Q. Text Res J 1993, 63, 706.
20. Ducoroy, L. J Appl Polym Sci 2007, 103, 3730.
21. Silverstein, R. M.; Clayton Bassler, G.; Morrill, T. C. Spectrometric Identification of Organic Compounds, 3rd ed.; Wiley: NY, 1975.
22. Gref, R.; et al. J Controlled Release 2006, 111, 316.