β-Cyclodextrin Stabilized on Three-Dimensional Polyester Fabric with Different Crosslinking Agents

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ABSTRACT: The stabilization of β-cyclodextrin (β-CD) on spacer polyester fabric (three-dimensional) is an interesting task. Using a crosslinking agent to stabilize β-CD on the spacer polyester fabric is necessary. This causes an increase in the durability of β-CD on the fabric. In this research, five different crosslinking agents, including two non-formaldehyde crosslinking agents (citric acid and 1,2,3,4-butane tetracarboxylic acid), one formaldehyde-based crosslinking agent (dimethylol dihydroxyl ethylene urea), and two different commercial siloxane-based softeners, were used to specify the best yield on the polyester spacer fabric with β-CD. The results showed that, among the different crosslinking agents, 1,2,3,4-butane tetracarboxylic acid provided the best durability after 10 washings. The changes in the weight, regain, drop absorption time on the fabric surface, metal-ion (chrome) absorption, and reactive-dye absorption were also reported, and scanning electron microscopy pictures were observed. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 210–217, 2010

Key words: β-cyclodextrin; polyester spacer fabric; crosslinking; stabilization; absorption; dyes/pigments; esterification; fibers; ion exchangers

INTRODUCTION

Spacer polyester fabric has a three-dimensional (3D) structure; it is produced by two separate fabrics through connecting threads (the threads create gaps between the two fabrics) with different bending hardnesses.[1,2] Among the characteristics of these fabrics, we can refer to the air circulation inside the fabric, flexibility, bending, and 3D appearance.[2] These types of textiles are technical textiles. Special applications of these fabrics include car seat covers, hospital mats, geotextiles, composites, sports equipment, medical clothing, and military uses.[3]

β-Cyclodextrins (β-CDs) are cyclic oligosaccharides containing seven units of D-glucose with Glucopiranozi (D-glucose or Glucopiranose) and they are netted through covalence bonds by C_1 and C_4 carbons.[4,5] They are produced during the destruction of saccharine by the CGTase enzyme.[6] CGTase can be obtained from different bases.[6] The β-CD molecule is in the form of a horn or sugar loaf with a molecular weight of 1135 and a height of 750–800 pm. The internal diameter of the molecule's hole is between 600 and 680 pm, and the external diameter is 1530 pm.[4,5,7] The volume of the hole is 260–265 Å^3, and the dissolution is 1.85 g/100 mL of water.[4–7] The internal section is hydrophobic in nature, and the external section is hydrophilic in nature.[6] These materials are stable in base solutions and are sensitive to acid hydrolysis. The stability of β-CDs against acid hydrolysis depends on the temperature and acidity. Therefore, cyclodextrins (CDs) are more stable at pHs above 3.5 and at temperatures above 60°C.[6]

β-CDs have a special structure and can be applied in finishing and dyeing processes.[8–11] Also, they can be used for the controlled release of perfumed materials and guest molecules from cavities, for a retardation effect in dyeing and finishing baths, for the absorption of smells, and for drug release in textile industries.[4,5,7–27]

Because fabrics are in direct contact with human skin, the toxic specifications of CDs have been studied.[6] The results indicate that they may be harmful to the human body in very high concentrations.[6] In November 13, 2000, β-CD was introduced as a food additive in Germany. With respect to Organization for Economic Co-operation and Development (OECD) experiments, this compound has no allergic impact.[12–14]

Szejtli et al.[17] reported the grafting of CDs onto cellulose fibers with epichlorohydrin as a crosslinking agent. Buschmann et al. claimed the incorporation of CDs into natural or synthetic materials by physical means or by chemical paths involving CD derivatives carrying aliphatic and aromatic groups, chlorocarboxylic acids, and chloroamino and dimethylol bifunctional compounds as linking agents.
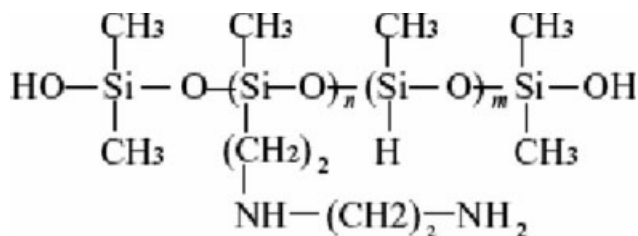
Figure 1 Chemical structure of the aminoethyl aminopropyl silicon softener (T.6).

Besides, Denter et al.[19] and Reuscher and co-workers[20,21] fixed a monochlorotriazinyl β-CD derivative onto different polymer materials, including cotton fibers. Furthermore, in a recent study, the possibility of fixing CDs permanently to cotton and wool fibers with poly(carboxylic acid)s (PCAs) as binding and crosslinking agents has been proposed.[22] Martel et al.[16] concluded that grafting occurred through the formation of a crosslinked copolymer between PCA and CDs. This copolymer was not covalently fixed to the fibers but physically adhered to or was entangled with the fibrous network. They remarked that grafting was resistant to washing.[16]

The efficiency of the copolymer created with crosslinking agents and CD depends on three factors: the curing temperature, curing time, and ratio of the crosslinking agents to the CD. According to the research results, the crosslinking agents interacts with CD on the fibers in a dry environment with thermal fixation above 140°C. The curing time has been also considered (at least 3 min for different types of dextrins).[16,23] Many researcher have worked on finishing regular fabric with β-CD; however, there is no report on the finishing of polyester spacer fabric with β-CD. Here, polyester spacer fabric was modified with β-CD and stabilized with different crosslinking agents. Moreover, the stability of β-CD on polyester spacer fabric was compared with various crosslinking agents.
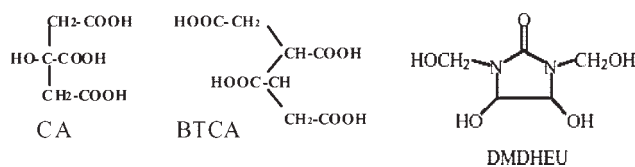
EXPERIMENTAL

Materials

The characteristics of 3D polyester fabric were as follows: a surface string of 150 den, a beneath string of 150 den, a monofilament connector string of 30 den,
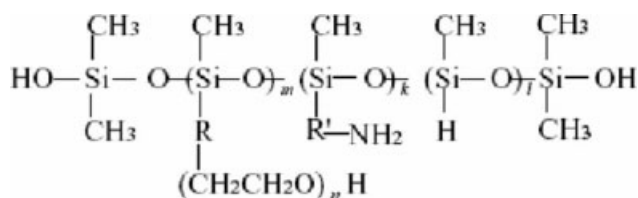
Figure 2 Chemical structure of the poly(ether amine) silicon softener (J.1).

Figure 3 Chemical structure of (a) CA, (b) BTCA, and (c) DMDHEU.

a weight of 255 g/m², and a thickness of 2–3 mm (Bonyad Polypropylene Fiber Production Co., Tehran, Iran). The other materials included 1,2,3,4-butane tetracarboxylic acid (BTCA), citric acid (CA), and sodium hypophosphite (Merck, Darmstadt, Germany), an aminoethyl aminopropyl poly(dimethyl siloxane) microemulsion (T.6; Fig. 1), a hydrophilic softener based on a poly(ether amine)-functional siloxane (J.1; Fig. 2), and a crosslinking agent based on dimethylol dihydroxyl ethylene urea (DMDHEU; Arman Chimi Afroz, Tehran, Iran). β-CD was purchased from Xl'an Hong Chang Pharmaceutical Co., Ltd. (Xi'an, Shaanxi, China).

PCAs are desirable bonders for providing bonding between finishing materials and fabrics. These material are used on the basis of their good esterification and for most pad–dry–cure systems that reduce the time of operation by means of catalysts. Sodium hypophosphite is often used as an appropriate catalyst, providing the best yield. PCAs react with the catalyst to take the form of a cyclic anhydride, and then they can react with functional groups of fabrics (Fig. 3).
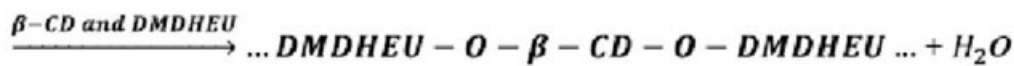
Experiments

First, fabric samples (20 × 10 cm²) were obtained, and then they were scoured with a nonionic detergent (1 g/L) at 60°C for 20 min. Then, the specified bath was prepared according to Table I. The fabric samples were then passed through the bath and padded with foulard with 100% wet pickup. The fabric was dried at 100°C for 4 min and then cured at 160°C for 3 min. The CA-treated samples were cured at 150°C and finally washed.
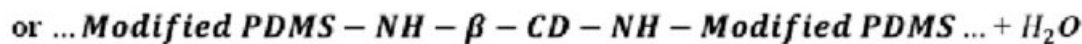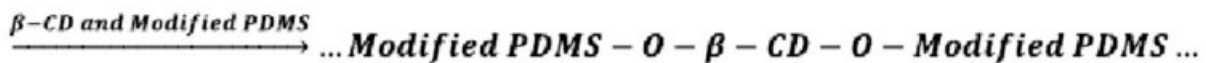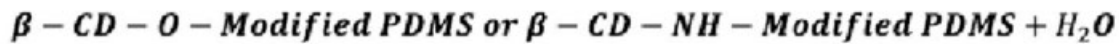
A Rotowash machine from Shirley (Lancashire, England) was used to determine the washing stability. A UV-2101 apparatus from Shimadzu (Kyoto, Japan) was used to determine the amount of

TABLE I
Specifications of Different Baths

Concentration of the crosslinking agent (g/L)	Catalyst (g/L)		β-CD (g/L)	Type of crosslinking agent
	CA	NaH₂PO₂		
100	–	20	100	CA
100	–	20	100	BTCA
30	20	–	100	J.1
20	20	–	100	T.6
100	15	–	100	DMDHEU

$$\beta - CD\ (-OH) + DMDHEU\ (= NCH_2OH) \xrightarrow{catalyst\ and\ heat} \beta - CD - O - DMDHEU + H_2O$$

$$\xrightarrow{\beta-CD\ and\ DMDHEU} ...DMDHEU - O - \beta - CD - O - DMDHEU\ ... + H_2O$$

a- Reaction between β-cyclodextrin and DMDHEU

$$\beta - CD\ (-OH) + Modified\ PDMS\ (-NH_2\ or - OH) \xrightarrow{catalyst\ and\ heat}$$

$$\beta - CD - O - Modified\ PDMS\ or\ \beta - CD - NH - Modified\ PDMS + H_2O$$

$$\xrightarrow{\beta-CD\ and\ Modified\ PDMS} ...Modified\ PDMS - O - \beta - CD - O - Modified\ PDMS\ ...$$

$$or\ ...Modified\ PDMS - NH - \beta - CD - NH - Modified\ PDMS\ ... + H_2O$$

b- Reaction between β-cyclodextrin and Modified PDMS

$$\beta - CD\ (-OH) + PCA\ (-COOH) \xrightarrow{catalyst\ and\ heat} \beta - CD - O - CO - PCA + H_2O$$

$$\xrightarrow{\beta-CD\ and\ PCA} ...PCA - O - CO - \beta - CD - O - CO - PCA\ ... + H_2O$$
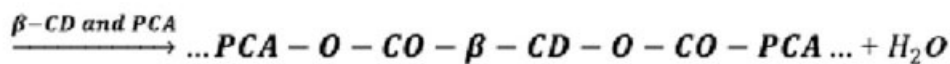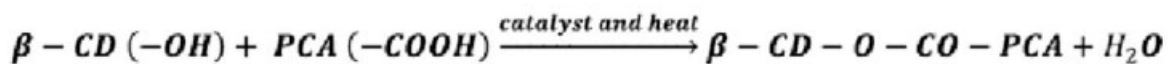
c- Reaction between β-cyclodextrin and PCA

Figure 4　Reaction between β-CD and different crosslinkers [PDMS = poly(dimethyl siloxane)].

absorption of chrome ions. A Varian Cary 500 (USA) was used to determine the amount of the reactive dye in the bath. For scanning electron microscopy (SEM), a LEO 440i was used to observe the fabric surfaces (Carl Zeiss, Jena, Germany).

Methods

Weight

The weights of the raw material and finished fabric after washing were measured. The weight change was calculated as follows:

$$\text{Weight change (\%)} = \frac{w_2 - w_1}{w_1} \times 100 \qquad (1)$$

where w_1 is the weight of the washed raw material and w_2 is the weight of the finished and washed fabric.

Regain

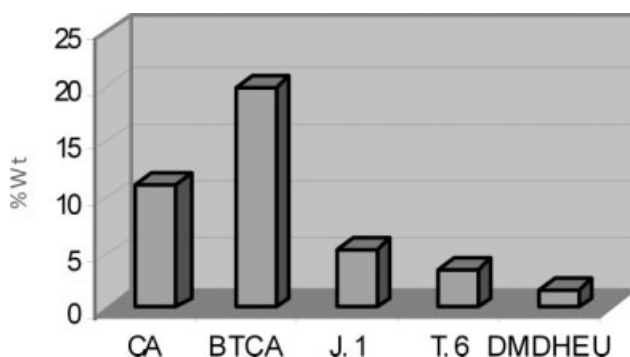This was determined according to AATCC Test Method 20A-1981 and calculated with the following formula:
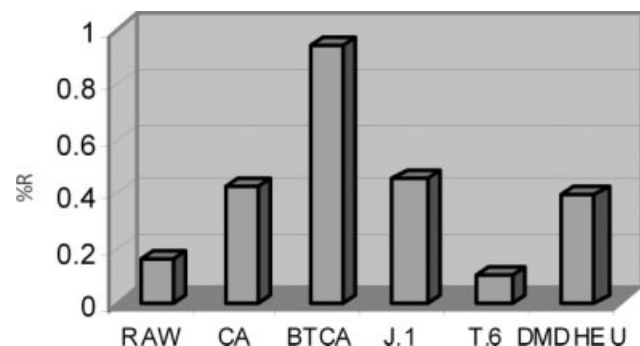

Figure 5　Weight gain for different samples.

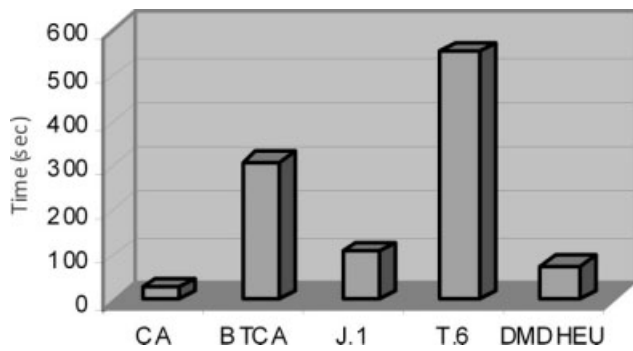**Figure 6**　Changes in the regain percentage (%R) for different samples.

Figure 7 Water drop absorption time for the finished fabric surfaces.

$$R\% = \frac{W - D}{D} \times 100 \qquad (2)$$

where W is the weight of the finished fabric after washing, D is the weight of the finished fabric after drying, and $R\%$ is the regain percentage.

Water drop absorption

This was determined according to AATCC Test Method 79-1995.

Chrome-ion absorption

A solution of potassium dichromate was prepared, and the samples were put in the solution for 2 h to adsorb metal ions. The amount of absorption was determined with a spectrophotometer. The absorption recipe for chrome ions was as follows: a fabric weight of 0.3 g, 20 mg of potassium dichromate, 120 min, and 22–24°C.

Reactive-dye absorption

The spacer polyester fabric was dyed with a reactive dye in this research. It is well known that polyester fabric has a compact structure with no functional groups to adsorb any dye. Polyester fabric is usually dyed with a disperse dye at a high temperature. Through the treatment of polyester fabric with β-CD, the hydroxyl groups are added to the polyester surfaces, providing functional groups for the reaction with reactive dyes; this is similar to the dyeing of cellulose with reactive dyes.

The dyeing recipe was as follows: 4% Remazol Blue RGB (reactive dye), 1 g of spacer polyester fabric, 1% owf sodium sulfate, an L:G ratio of 40 : 1, 80°C for 60 min, washing with cold water, washing with warm water, and general washing with a nonionic detergent (1 g/L) and sodium carbonate (1 g/L) at 60°C for 30 min.

Durability after repeated washing

The finished fabric was washed three times with a cyclic washing machine according to AATCC Test Method (2A)-1996.

RESULTS AND DISCUSSION

Different crosslinking agents have various reactive groups that can react with hydroxyl groups of β-CD. In this way, the crosslinking agents and β-CD can produce a layer of crosslinked β-CD on the fabric surface. They may react with available hydroxyl and carboxyl groups of polyester fabrics. The mechanism of the reaction of β-CD with different crosslinking agents is proposed in Figure 4. This can be done through chemical and physical reactions that lead to the formation of a copolymer. This copolymer can be retained on the polyester fabric surface; it modifies the polyester structure and creates special characteristics in the product.

The changes in the fabric weight are illustrated in Figure 5. All the crosslinking agents increased the fabric weight. This means that all the crosslinking agents could create a copolymer with β-CD on the fabric surface. However, the rates of crosslinking were different for the various crosslinking agents. The highest weight gain was for sample 2, in which β-CD and BTCA had the highest concentrations. The sample with CA and β-CD was second-order. This means that BTCA with four carboxyl groups reacted with hydroxyl groups of β-CD better than CA with
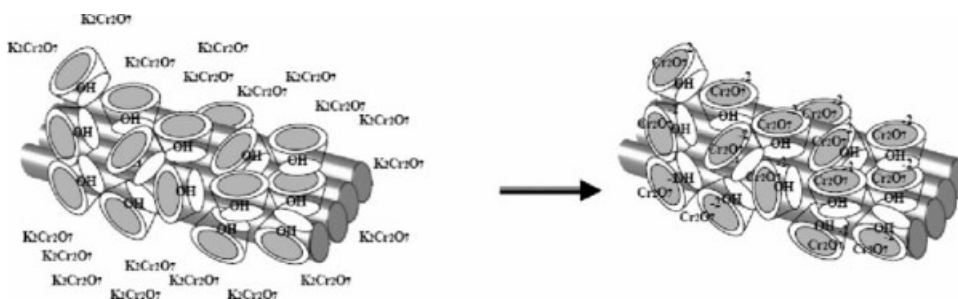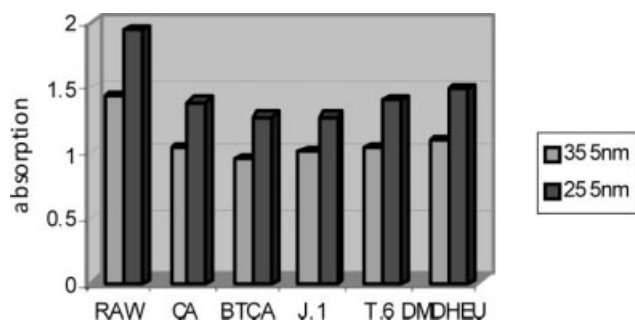

Figure 8 Schematic of chrome-ion adsorption by the β-CD-treated polyester fabric.

Figure 9 Absorption in the remaining bath containing chrome ions.

three carboxyl groups. The polyester sample treated with DMDHEU and β-CD experienced the least weight gain. The order of the weight gain for the different samples was as follows:

Sample treated with BTCA > treated with
CA > Sample treated with J.1 > Sample treated with
T.6 > Sample treated with DMDHEU

The changes in regain for different samples are presented in Figure 6. It can be concluded that the regain could be changed after finishing with β-CD and different crosslinking agents. The highest regain change (%) was obtained for sample 2, which had the highest concentrations of β-CD and BTCA. The sample treated with CA experienced less change than the sample treated with BTCA. This agreed with the weight gain as BTCA led to higher weight gain. This could be ascribed to the increasing number of carboxyl groups of BTCA increasing the regain. The lowest regain was found for the sample treated with T.6, which has fewer hydroxyl groups than J.1. The sample treated with T.6 had less weight gain than the sample treated with J.1. These results confirm the lower interaction between T.6 and β-CD in comparison with J.1 and β-CD. The sample

treated with DMDHEU experienced improved regain. This could be attributed to the hydroxyl groups of DMDHEU. However, the weight gain was low for this sample. The order of increasing regain for the various samples was as follows:

Sample treated with BTCA > Sample treated
with J.1 > Sample treated with CA > Sample treated
with DMDHEU > Sample treated with T.6

The time of water drop absorption on the fabric surface can be observed in Figure 7. The time was delayed for the sample treated with T.6 and β-CD. The water drop adsorbed onto the untreated sample very quickly. The highest time of water adsorption belonged to the sample treated with T.6. This can be related to the hydrophobic structure of this siloxane softener. The results agreed with the results for regain as the lowest regain belonged to the sample treated with T.6. Water absorption and spreading on fabric surfaces depend on the hydrophilic groups on the fabric surface and porosity of surface for wicking. The treatment of a polyester with crosslinking agents and β-CD may interfere with the wicking process by blocking some of the interyarn and interfiber pores. This could be the reason for the reduced rate of water adsorption on the treated samples. The increasing order of time drop absorption for the samples was as follows:

Sample treated with T.6 > Sample treated with
BTCA > Sample treated with J.1 > Sample treated
with DMDHEU > Sample treated with CA

The polyester fabric treated with β-CD and various crosslinking agents could adsorb metal ions in the β-CD cavity. On this basis, a schematic of chrome-ion adsorption by β-CD on polyester fabric is shown in Figure 8. The results for the absorption of a chrome-ion bath after the treatment of the samples are
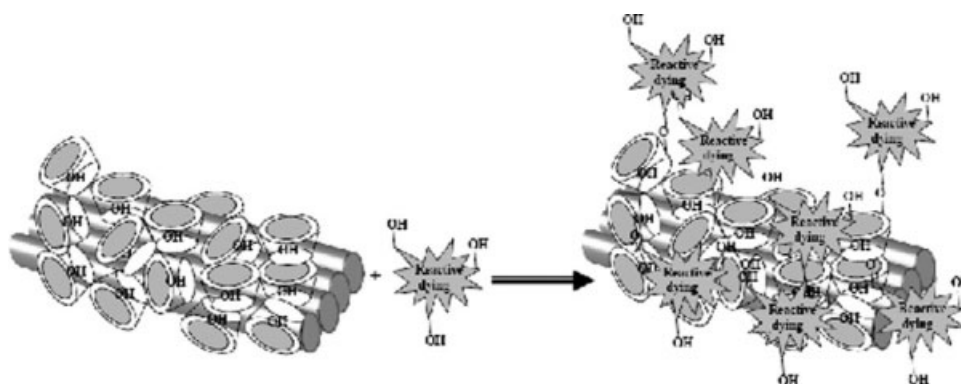
Figure 10 Schematic of the reaction of the reactive dye on the β-CD-finished polyester fabric.
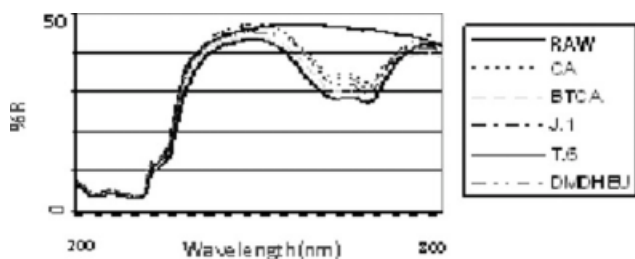
Figure 11 Reflectance percentage (%R) of the β-CD-treated fabric after dyeing with the reactive dye.

illustrated in Figure 9. It can be concluded that the absorption of chrome ions varied for the different samples after the samples remained at room temperature for 2 h. The greatest amount of absorption belonged to the raw sample as few chrome ions were adsorbed by the fabric sample. The lowest absorption belonged to the fabric sample treated with BTCA and β-CD. This means that this sample had higher potential for chrome-ion adsorption. The order of chrome-ion adsorption for the different samples was as follows:

Sample treated with BTCA > Sample treated with
J.1 > Sample treated with CA > Sample treated with
T.6 > Sample treated with DMDHEU

The reactive dye could react with hydroxyl groups of β-CD. When the polyester fabric was treated with β-CD and different crosslinking agents, then it was composed of hydroxyl groups that could react with the functional groups in the reactive dyes. A schematic of the reaction of the reactive dye with the β-CD-finished polyester fabric is displayed in Figure 10. The samples dyed with the reactive dye were blue. The reflectance spectrum of the dyed samples is illustrated in Figure 11. It can be observed that the spectrum of the raw fabric is completely different from the other spectra. This means that the β-CD-treated fabric was capable of dying with the
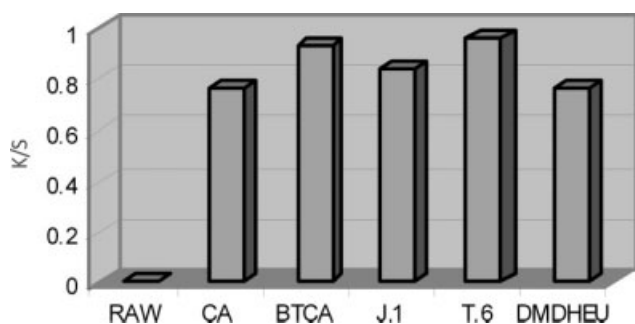
reactive dye, and all the treated fabrics adsorbed and reacted with the reactive dye. The reflectance spectrum of the treated fabric showed a big peak around 500–600 nm. This confirmed the ability of the β-CD-treated polyester to be dyed with the reactive dyes. The K/S values for the treated and dyed fabrics (where K is the absorption coefficient and S is the scattering coefficient) are presented in Figure 12. The adsorption of the reactive dye by different samples showed K/S values between 0.7 and 0.9. This indicated that all the β-CD-treated polyester fabrics could adsorb and react with the reactive dye. Also, it can be proposed that the type of crosslinking agent has little influence on the reactive dyeing of β-CD-treated polyester fabric. However, crosslinking agents with hydroxyl groups may increase the reactive dyeing. The order of the adsorption of the reactive dye on different polyester fabrics was as follows:

Sample treated with T.6 > Sample treated with
BTCA > Sample treated with J.1 > Sample treated
with CA > Sample treated with DMDHEU

The results for the durability of finished materials on the differently treated polyester fabrics are shown in Figure 13. The most finished material remained on the fabric sample treated with β-CD and BTCA after 10 washings. The CA-treated fabric had lower durability than the BTCA-treated fabric. This means that BTCA with four carboxyl groups has a higher potential for reacting with β-CD and remaining on the fabric surface. The durability of the samples treated with the siloxane-based softener was lower than that of the PCA-treated samples. This indicates the lower reactivity of the siloxane-based softener with β-CD. The owest durability belonged to the DMDHEU-treated sample. The order of the materials removed from the finished samples after 10 washings was as follows:

Figure 12 K/S values of differently treated samples.
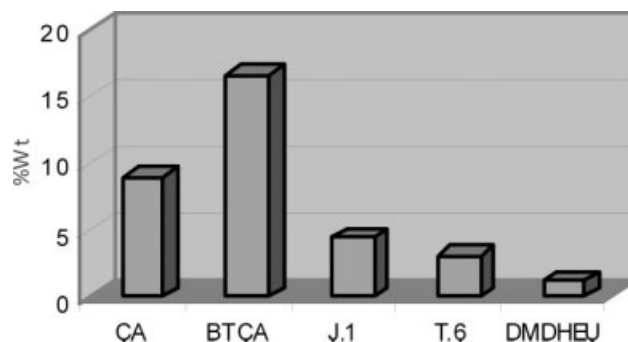
Figure 13 Amounts of the finished materials on the fabric after 10 washings.
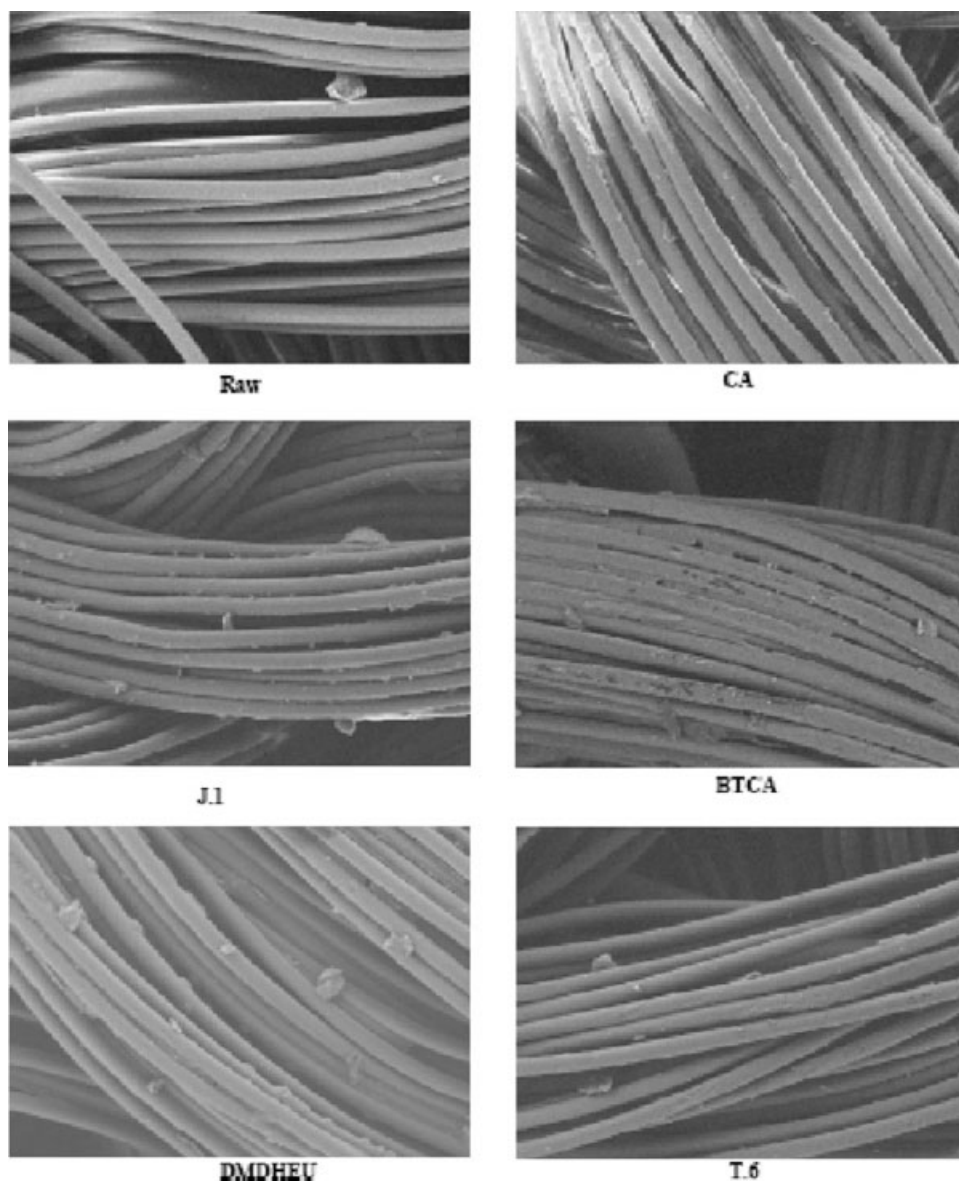
Figure 14   SEM pictures of differently treated samples.

Sample treated with BTCA > Sample treated with
CA > Sample treated with J.1 > Sample treated with
DMDHEU > Sample treated with T.6

SEM pictures of the raw polyester fabric and fin-
ished fabrics are presented in Figure 14. The fiber
surface was flat for the raw fabric, but a slight
change occurred when the fabric was treated with
different crosslinking agents. The surface of the
fibers in all the treated fabrics contained finishing
material. However, the amount of the finishing
material varied for the different samples. The most
changes could be seen in the sample treated with
BTCA, and the fewest changes were found for the
DMDHEU-treated sample. The surface of the CA-
treated sample contained added finishing agents.

However, the amounts of the finishing agents were
lower for the CA-treated sample versus the BTCA-
treated sample. The SEM pictures confirmed the
results for the weight gain.

CONCLUSIONS

The modification of spacer (3D) polyester fabric is
important for increasing its applications. This
research has shown that β-CD is a compatible natu-
ral material with external hydroxyl groups and
internal hydrophobic cavities that can produce 3D
polyester fabric with new specifications. To improve
the stability of β-CD on the fabric, different cross-
linking agents can be used; these may react with the
hydroxyl groups of β-CD. This research has shown
that a β-CD-modified fabric can be produced with
good stability after 10 washings. Also, the 3D

polyester fabric can be dyed with reactive dyes after treatments with β-CD and crosslinking agents. Furthermore, the treated fabric can adsorb chrome ions as an attractive fabric. This research work has shown that five different materials can be used as crosslinking agents (CA, BTCA, J.1, T.6, and DMDHEU) for finishing polyester fabric. Among the different crosslinking agents, the best yield was found when BTCA was used for finishing 3D polyester fabric.

References

1. Kunde, K. Melliand Textilber Int Text Rep 1995, 65, 299.
2. Hsieh, L. Text Res J 1995, 65, 299.
3. Heide, M.; Zschenderlein, D.; Mohring, U. Presented at the 4th International Conference of Innovation and Modeling of Clothing Engineering Processes: Maribor, Slovenia, 2003.
4. Voncina, B.; Vivod, V.; Jausovec, D. Dyes Pigments 2007, 74, 642.
5. Vogtle, F. Supramolecular Chemistry: An Introduction; Wiley: New York, 1991.
6. Martin Del Valle, E. M. Process Biochem 2004, 39, 1033.
7. Weber, E. Top Curr Chem 1987, 140, 1.
8. Savarino, P.; Viscardi, G.; Quagliotto, P.; Montoneri, E.; Barni, E. Dyes Pigments 1999, 42, 143.
9. Szejtli, J. Pure Appl Chem 2004, 76, 1825.
10. Szejtli, J. Starch 2003, 55, 191.
11. Szetjli, J. Chem Rev 1998, 98, 1743.
12. Hedges, R. A. Chem Rev 1998, 98, 2035.
13. Irie, T.; Uekama, K. J Pharm Sci 1997, 86, 147.
14. Loftsson, T.; Brewster, M. E. J Pharm Sci 1996, 85, 1017.
15. Eastburn, S. D. Biotechnology 1994, 12, 325.
16. Martel, B.; Morcellet, M.; Ruffin, D.; Ducoroy, L.; Weltrowski, M. J Inclusion Phenom Macrocycl Chem 2002, 44, 443.
17. Szejtli, J.; Zsadon, B.; Fenyvesi, E.; Horvarth, O.; Tudos, F. U.S. Pat. 4,357,468 (1982).
18. Buschmann, H. J.; Denter, U.; Knittel, D. J of The Textile Institute 1988, 89, 554.
19. Denter, U.; Schollmeyer, E. Proc Int Cyclodextrins Symp 1996, 8, 559.
20. Reuscher, H.; Hirsenkron, R.; Hass, W. Eur. Pat. EP 069741A1 (1995).
21. Denter, U.; Schollmeyer, E. Proc Int Cyclodextrins Symp 1996, 8, 553.
22. Martel, B.; Weltrowski, M.; Ruffin, D.; Morcellet, M. J Appl Polym Sci 2002, 83, 1449.
23. Martel, B.; Morcellet, M.; Ruffin, D.; Vinet, F.; Weltrowski, M. J Inclusion Phenom Macrocycl Chem 2002, 44, 439.
24. Ducoroy, L.; Martel, B.; Bacquet, B.; Morcellet, M. J Inclusion Phenom Macrocycl Chem 2007, 57, 271.
25. Ducoroy, L.; Martel, B.; Bacquet, B.; Morcellet, M. J Appl Polym Sci 2007, 103, 3730.
26. Lee, M. H.; Yoon, K. J.; Ko, S. E. J Appl Polym Sci 2000, 78, 1986.
27. Martel, B.; Ruffin, D.; Weltrowski, M.; Leckhiri, Y.; Morcellet, M. J Appl Polym Sci 2005, 97, 433.