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Cotton fabric finished with β-cyclodextrin: Inclusion ability toward antimicrobial agent

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ABSTRACT

β-Cyclodextrin was grafted onto cotton fabric through crosslinking with butane tetracarboxylic acid in presence of sodium hypophosphite monohydrate as a catalyst. This finished cotton fabric was loaded with the antimicrobial agent octenidine dihydrochloride. β-Cyclodextrin-grafted cotton fabrics, both after loading with octenidine dihydrochloride or before loading (control) were characterized for their antimicrobial activity against two types of bacteria (Gram positive and Gram negative) and two types of fungi, using the Diffusion Disk Method. The antimicrobial cotton fabric was subjected to several washing cycles and the antimicrobial activity was measured after each washing cycle to examine the durability of this antimicrobial finishing against repeated washing. The measurements showed that the finished cotton fabrics retain reasonable deal of their antimicrobial activity, even after 20 washing cycles. This long-lasting antimicrobial activity is attributed to the hosting ability of the cavities present in cyclodextrin moieties, which host the antimicrobial agent molecules and release them gradually.

1. Introduction

The family of chemical compounds known, as cyclodextrins are group of oligosaccharides in a cyclic form. These cyclic oligosaccharides are arranged in cone shape arrangement composed of at least five glucopyranose units which are bonded together covalently through carbon number one and carbon number four (Baudin, Camara, & Navaza, 2007; Puliti, Mattia, & Paduano, 1998). Each glucopyranose unit in the cyclodextrin molecule have three hydroxyl groups, which are free for interaction and each of them has its own reactivity. The lower and upper faces of the torus-shaped cavity contain secondary and primary hydroxyl groups (Szejtli, 1988). These hydroxyl groups are oriented outside the cavity and the oxygen atoms of the glycosidic bonds are inside the cavity, which makes the environment in the cavity interior very rich in electrons (Ouziel & Kulke, 2007). The distribution of the hydroxyl groups below and upper the cavity, makes the exterior of the cavity hydrophilic in nature, while the concentration of the oxygen electrons inside the cavity makes the interiors of cyclodextrins hydrophobic in nature (Dodziuk, 2006), that is why cyclodextrins have high ability to host a large variety of hydrophobic compounds inside their cavities and this inclusion ability is aided by means of complexation mechanism between the host cavity and the guest molecules (Abdel-Halim, Fouda, Hamdy, Abdel-Mohdy, & El-Sawy, 2010; Abdel-Halim et al., 2011; Shao, Martel, Morcellet, Weltrowski, & Crini, 1996).

The cyclodextrin having seven glucopyranose units and known as β-cyclodextrin is the most common and commercially available type of cyclodextrins (Scheme 1). This is because of ease of synthesis and reasonable prices. In the structure of β-cyclodextrin, the cavity is surrounded by the hydroxyl groups from the upper and down sides, while the loan pairs of electrons of the oxygen atoms in the glycosidic bonds are directed to the interior of the cavity, giving rise to rich electron density inside the cavity, thus making the cavity interior is relatively hydrophobic, while the exterior of the cavity is hydrophilic due to the high availability of the hydroxyl groups (Del Valle, 2004). Due to this high hosting and inclusion ability resulting from the difference in the hydrophilicity of the exterior and the interior, cyclodextrins can form inclusion complexes and host a wide variety of compounds. These types of inclusion complexes lead to change in the physical properties of the substances to be hosted by cyclodextrin cavities, and these phenomena found wide variety of applications like the encapsulation characterized by controlled release of the hosted substances, like drugs, flavoring agents, fragrances and pesticides (Ishiwata & Kamiya, 1999; Nguyen, Liu, Zhao, Thomas, & Hook, 2013; Pedersen, Bjerregaard, Jacobsen, & Sørensen, 1998; Veiga & Ahsan, 2000). Inclusion ability of cyloodextrin gives high benefits and presents easy solutions for some problems facing people in some applications like for example, the high solubility of some molecule in aqueous media, which can be controlled through hosting as a guest molecule in cyclodextrin cavity in order to release them gradually. Another example is

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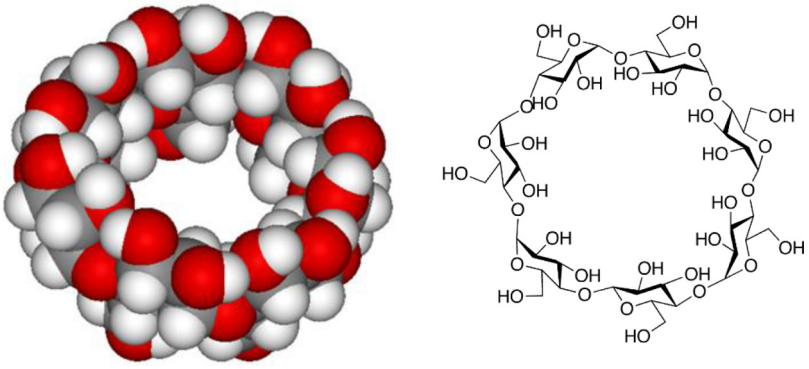


Scheme 1. Structure of β-cyclodextrin (β-CD).

the controlled release of the highly volatile guest molecules, upon hosting in cyclodextrin cavity. This is in addition to protecting some molecules against some factors like oxidation and thermal or chemical degradation, when hosted inside cyclodextrin cavity (Ghosh, Biswas, & Ghosh, 2011; Li & Xu, 2010; Wang, Cao, Sun, & Wang, 2011; Yamamoto, Kurihara, Mutoh, Xing, & Unno, 2005).

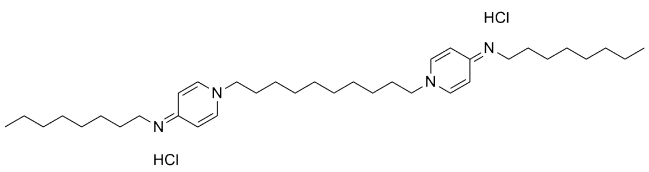
The natural polymer cellulose, which comes from renewable resource, is considered one of the most important natural polymers on earth due to its abundance. As a natural polymer, cellulose is an environmentally friendly polymer, biocompatible and in addition to that, cellulose is easily modified to a wide variety of cellulose derivatives useful in unlimited number of applications. All these features make cellulose a promising source of raw material for industry in the future as a substituent to other exhaustible resources. Cotton fabric has excellent performance properties like high hydrophilicity and high capability to discharge static electricity, which make cotton fabric very comfortable for wear compared to other synthetic fabrics like polyester and acrylic fabrics. In its native state, cotton fabric is composed of more than 95% cellulose and the rest is noncellulosic materials like pectin, hemicelluloses, natural waxes and oils, in addition to coloring matters. In order to make cotton fabric ready for different finishing processes and dying with different shades, gray cotton fabrics must undergo some chemical pretreatments to increase its water absorbency and remove coloring matter and make the fabric ready for light shade dyeing. These pretreatments involve scouring (Abdel-Halim, Fahmy, & Fouda, 2008; Abdel-Halim, Konczewicz, Zimniewska, Al-Deyab, & El-Newehy, 2010; Agrawal, Nierstrasz, & Warmoeskerken, 2008; Peng, Gao, Sun, Yao, & Qiu, 2009; Tanapongpipat, Khamman, Pruksathorm, & Hunsom, 2008), bleaching (Abdel-Halim, 2012a, 2012b, 2013; Abdel-Halim & Al-Deyab, 2011, 2013; Basto, Tzanov, & Cavaco-Paulo, 2007; Mistik & Yükseloglu, 2005; Tian, Branford-White, Wang, Nie, & Zhu, 2012) and finishing (Abdel-Halim, Abdel-Mohdy, Al-Deyab, & El-Newehy, 2010; Fahmy & Abdel-Halim, 2010; Mohsin, Rasheed, Farooq, Ashraf, & Shah, 2013; Teli, Sheikh, & Bhavsar, 2013; Xiao, Zhang, Yang, & Huang, 2007; Yang & Yang, 2005).

Recently, many routes and procedures have been developed to increase the functionality of cotton fabrics and to produce fabrics known as smart fabrics. A very famous procedure to produce cotton smart fabric is to modify cotton fabric with cyclodextrin through grafting/crosslinking and apply the so obtained functionalized cotton in different areas (Desmet, Takács, Wojnárovits, & Borsa, 2011; Scalia et al., 2006; Vismara, Melone, Gastaldi, Cosentino, & Torri, 2009; Wang & Cai, 2008). Cyclodextrin can be applied to the fabric either physically by immersing the fabric in cyclodextrin solution to give temporary finishing effect or chemically by fixing the cyclodextrin on the fabric surface through formation of chemical bonds to give permanent finishing effect (Buschman, Denter, Knittel, & Schollmeyer, 1998; Murthy & Shown, 2009). The use of cyclodextrins derivatives in different textile applications has attracted the attention of many researchers and new approaches for hosting varying molecules inside cyclodextrin cavities have been reported (Denter, Buschmann, Knittel, & Schollmeyer, 1997; Szejtli, 2003). Some of the researches reported the improvement in finishing ability and dye ability of cyclodextrin-finished fabrics (Savarino, Viscardi, Quagliotto, Montoneri, & Barni, 1999; Voncina & Le Marechal, 2005; Wang & Chen, 2006). Others reported the ability of resin-finished cotton in the presence of cyclodextrins to capture the bad perspiration smell (Buschmann, Knittel, & Schollmeyer, 1991) or to control the release of antibacterial agents (Voncina & Majcen, 2004).

Topical disinfectants are broad spectrum antimicrobial agents, which are used for disinfecting skin contaminated wounds and mucous membranes. Octenidine dihydrochloride (octenidine) (Scheme 2) is considered a unique antimicrobial agent that can penetrate the cell wall and form chemical complexes with the cell components resulting in killing the bacterial cells, that is why octenidine dihydrochloride has high antimicrobial activity.

The chemical structure of octenidine dihydrochloride is bis-(dihydropyridinyl)-decane derivative. It is a kind of cationic surfactants which is used for disinfection as an aqueous solution of concentrations 0.1–2.0%. Its antimicrobial action is quite similar to the action of quaternary ammonium compounds, abbreviated quats but octenidine dihydrochloride has broader spectrum of activity toward both Gram positive and Gram negative bacteria (Dogan et al., 2008; Kramer & Assadian, 2013; Krishna & Gibb, 2010). Many countries in Europe use octenidine dihydrochloride to replace quaternary ammonium compounds or chlorhexidine derivatives. Octenidine dihydrochloride is generally used for disinfection purposes in aqueous solutions, where 2-phenoxyethanol is added to increase its disinfection potential (Stahl, Braun, Siebert, & Kietzmann, 2010).

The aim of the present work is to impart antimicrobial activity to cotton fabric. This is achieved by grafting β-cylodextrin onto cotton fabric by use of butane tetracarboxylic acid as cross linking agent, through formation of ester linkage between the carboxyl groups of the polycarboxylic acid and the hydroxyl groups of both cellulose and cyclodextrin. The cavities of β-cylodextrin fixed on the cotton



Scheme 2. Structure of octenidine dihydrochloride (OCT).

fabric surface will be loaded by the antimicrobial agent octenidine dihydrochloride to impart antimicrobial activity to the cotton fabric. The durability of the antimicrobial activity of the treated cotton fabric will be evaluated after repeated washing cycles.

2. Experimental

2.1. Materials and chemicals

Bleached plain weave cotton fabric (147 g/m^2) was kindly supplied by Misr Company for Spinning and Weaving, Mehalla El-Kobra, Egypt. The fabric was subjected to more purification in the laboratory by treatment at the boil for 60 min in an aqueous solution of sodium carbonate (2 g/l, w/v) and the non-ionic wetting agent Marlipal O13/80 (2 ml/l, v/v), then the fabric was washed well with water and air-dried.

β-Cyclodextrin (β-CD) and 1,2,3,4-butanetetracarboxylic acid (BTCA) were supplied by Sigma–Aldrich. All other chemicals were laboratory grade reagents.

2.2. Grafting of β-CD onto cotton fabric

β-CD wax fixed onto the cellulosic fabric according to the method described by Medronho et al. (2013). Cotton fabric sample (30 cm × 30 cm) was immersed in an aqueous solution of β-CD, 5–20% (w/v) and BTCA, 6% (w/v) together with the catalyst sodium hypophosphite monohydrate (SHP), 1% (w/v). The pH value of the treatment solution was always adjusted to 2.7 before immersing the fabric. The fabric was padded to a wet pick up of 100%, dried in an air oven at 110 °C for 5 min. The cross linking of β-CD to the cotton fabric via esterification with the polycarboxylic acid was affected by curing the dry fabric at different curing temperature (150–180 °C) for 90 s. After curing, the textile fabric was washed thoroughly with hot distilled and left to dry at room temperature overnight.

2.3. Estimation of graft yield

To evaluate the gain in fabric weight due to the finishing treatment (graft yield) the air-dried treated sample and cotton sample without any finishing were dried in an air oven at 105 °C for 3 h, cooled in a desiccator and weighed. This process is repeated until two successive weights are the same.

The percent graft yield (GY) is calculated from the equation

$$\%GY = \frac{W_2 - W_1}{W_2} \times 100$$

where W_2 is the dry weight of the grafted fabric sample and W_1 is the dry weight of fabric sample before grafting.

2.4. Estimation of fabric performance properties

The dry wrinkle recovery angle of the treated and untreated cotton fabrics was measured according to the ASTM method D-1296-98. Fabric's tensile strength, either the finished fabric sample or the untreated fabric was tested in the warp direction and the weft direction according to the ASTM method D-2256-98. The wettability of the fabrics was estimated according to a reported method (Arbeitsgruppe, 1987). CIE whiteness index of the finished and untreated fabrics was measured according to the standard AATCC test method number 110-1989.

2.5. Inclusion of octenidine dihydrochloride inside grafted cotton fabrics

β-CD-grafted cotton fabric and control cotton fabrics were dipped, separately, at room temperature for 60 min in aqueous solution containing 1% (w/v) octenidine dihydrochloride (OCT) (broad-spectrum antimicrobial agent). The immersion was carried out using a material to liquor ratio of 1:20. The samples were then padded to wet pick-up of 100% and then washed twice with double distilled water to get rid of the adsorbed OCT from the cotton fabric surface, which is not hosted by the β-CD cavities.

2.6. Estimation OCT hosted by β-CD cavities

Ultra violet-high performance liquid-chromatography (UV-HPLC) was the tool used for analyzing the concentration of OCT, extracted from the loaded cotton fabric. The HPLC instrument used was equipped with the auto sampler 508, Beckmann and the UV-VIS-detector 168, Beckman. The mobile phase used for detecting OCT was composed of 80% methanol and 20% citric acid/disodium hydrogen phosphate buffer solution of pH 2.2 and the wavelength for OCT detection was 280 nm.

2.7. Estimation of antimicrobial activity for finished cotton fabric

Diffusion Disk Method was used in this paper for estimating the antimicrobial activity for finished and control cotton fabrics (Irob, Young, & Apderson, 1996). The two fungus (*Candida albicans* and *Aspergillus flavus*) and the two bacteria (*Escherichia coli* and *Staphylococcus aureus*) were selected in this study to examine the antimicrobial activity of the finished cotton fabrics loaded with OCT and the durability of this antimicrobial activity after repeated washing cycles. The percent retention of antimicrobial activity after washing is, to what extent the fabric is able to exhibit antimicrobial activity after repeated washing and is expressed by the equation given below.

$$\%\,\text{antimicrobial activity retention} = \frac{A_2}{A_1} \times 100$$

where A_1 is the estimated antimicrobial activity before washing and A_2 is the estimated antimicrobial activity after washing.

2.8. Washing of antimicrobial cotton fabric

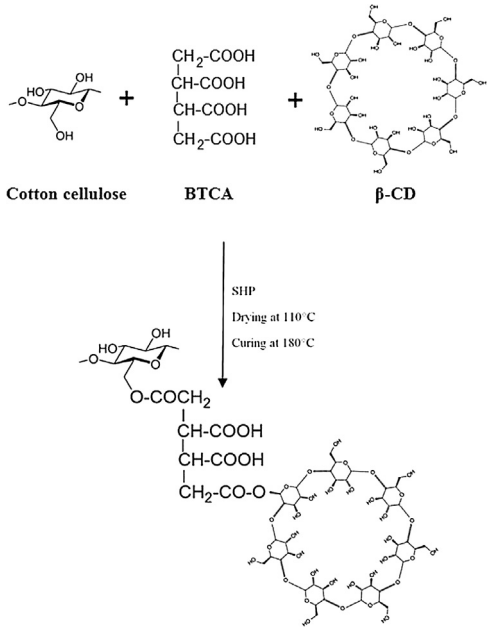
β-CD-grafted cotton fabric loaded with OCT were subjected to repeated washing/drying cycles. Washing was carried out using an aqueous solution of 2 g/l sodium carbonate and 2 ml/l Marlipal O13/80 non-ionic wetting agent at 60 °C for a duration of 15 min using material to liquor ratio of 1:20. After each washing cycle, the fabric was dried and the antimicrobial agent was estimated after each washing cycle in order to determine the number of washing cycles, after which the fabric loses its antimicrobial activity.

3. Results and discussion

3.1. Grafting of β-CD onto cotton fabric

3.1.1. Mechanism

BTCA is a polycarboxylic acid that has four carboxylic groups, which are capable of forming ester linkages with hydroxyl groups of both cotton cellulose and β-CD thus binding the β-CD to the cotton fabric through the formed ester linkage with BTCA. Scheme 3 illustrates the esterification reaction thus, cotton cellulose is treated by an aqueous solution of BTCA and β-CD in presence of SHP as a catalyst, followed by padding to a wet pick up of 100%. Upon drying at 110 °C, the carboxyl groups of BTCA are in the



Scheme 3. Mechanism of β-CD grafting onto cotton fabric.

vicinity of the hydroxyl groups of cellulose and β-CD, but so far no esterification reaction took place yet. Upon curing the treated cotton fabric at 180 °C, H_2O molecules are removed as a result of esterification reaction and ester linkage are formed between BTCA and both cellulose and β-CD, resulting in grafting β-CD onto cellulose through this ester linkage.

3.1.2. Effect of β-CD concentration on the graft yield

Cotton fabric samples (10 g each) were immersed on finishing solutions containing different concentrations of β-CD, namely, 5%, 10%, 15% and 20%, each together with 6% BTCA and 1% SHP. After immersion for 5 min, the fabrics were padded to a wet pick up of 100%, dried at 110 °C for 5 min and then cured for 90 s at 180 °C. Fig. 1 shows the effect of varying the β-CD concentration on its amount fixed onto the cotton fabric or the graft yield. The figure shows that increasing the concentration of β-CD is always accompanied by increase in the graft yield. However at low β-CD concentration (5%), it is noticed that only 10% of the β-CD picked up by the fabric was fixed during the curing step and the rest (90%) washed out during the washing step. Increasing the concentration of β-CD to 10% in the finishing solution, it is noticed that 30% are fixed and 70% are washed out. In case of using 15% β-CD, it is noticed

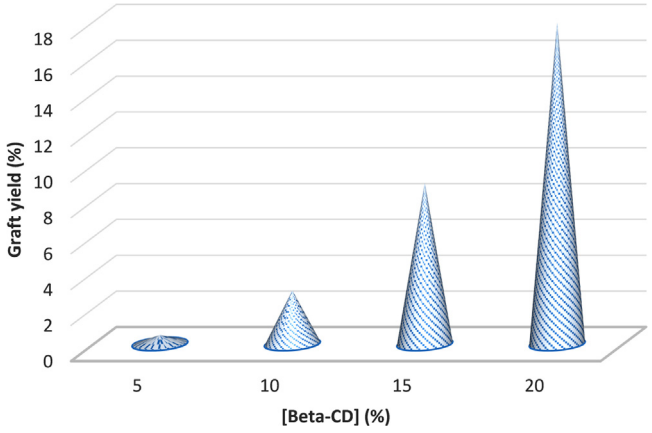


Fig. 1. Effect of β-CD concentration on the graft yield.

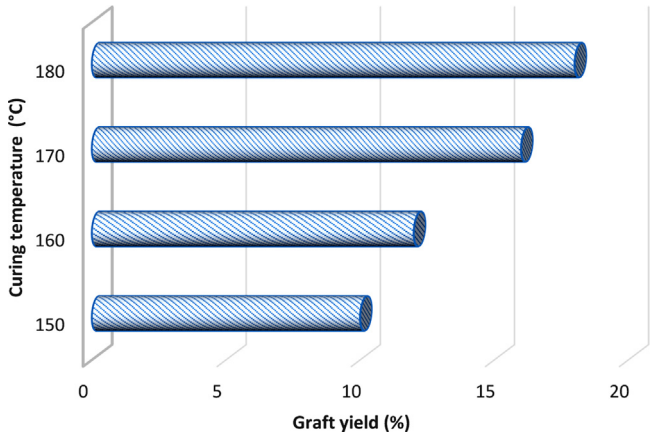


Fig. 2. Effect of curing temperature on the graft yield.

that 60% are fixed and 40% are washed out. Finally the best fixation result was obtained when the β-CD concentration in the finishing solution was 20%, where 90% of the β-CD are fixed and 10% only are washed out. The low percent fixed β-CD at 5% β-CD concentration is because at this low concentration and due to the dilution effect, the β-CD molecules are not in the vicinity of BTCA molecules which may decrease the efficiency of the esterification reaction and accordingly no β-CD will be bonded to the cotton fabric. The reverse holds true, that as the β-CD concentration increases, there is more crowding and more β-CD molecules will be in the vicinity of BTCA molecules, giving rise to high esterification efficiency and accordingly more β-CD molecules bonded to the cotton fabric.

3.1.3. Effect of curing temperature on the graft yield

Four cotton fabric samples (10 g each) were immersed on finishing solutions containing β-CD, 20%, together with 6% BTCA and 1% SHP. After immersion for 5 min, the fabrics were padded to a wet pick up of 100%, dried at 110 °C for 5 min. The four padded samples are cured for 90 s and each one was cured at certain curing temperature, one sample at 150 °C, the second sample at 160 °C, the third sample at 170 °C and the fourth sample at 180 °C. Fig. 2 shows the effect of curing temperature on the percent graft yield. It is clear from the figure that the graft yield increases by increasing the curing temperature and this is logic because the high temperature favors the esterification reaction that the water molecules are removed faster and the reaction is shifted in the direction of ester formation. On the other hand, curing temperature of 160 °C was found to be optimum curing temperature because at higher temperatures the cotton fabrics showed undesirable yellowness.

3.1.4. Effect of β-CD concentration on fabric's performance properties

Table 1 shows the effect of the variation in β-CD concentration on the performance properties of the finished cotton fabric samples. It is clear from the table that increasing the concentration of

Table 1
Effect of β-CD concentration on fabric's performance properties.

[β-CD] (%)	Wrinkle recovery angle, warp + weft (°)	Tensile strength (kg)	Whiteness index	Wettability (s)
5	135	59.5	78	2
10	159	57.3	75	2
15	178	55.3	73	2
20	190	53.9	73	2
Untreated	121	63.2	80	1

BTCA, 6% (w/v); SHP, 1% (w/v); pH 2.7; wet pick up of 100%; drying at 110 °C for min; curing temperature 180 °C; curing time 90 s.

Table 2
Effect of curing temperature on fabric's performance properties.

Curing temperature (°C)	Wrinkle recovery angle, warp + weft (°)	Tensile strength (kg)	Whiteness index	Wettability (s)
150	125	61.1	79	2
160	138	59.3	76	2
170	167	56.3	74	2
180	190	53.9	73	2
Untreated	121	63.2	80	1

β-CD, 20%; BTCA, 6% (w/v); SHP, 1% (w/v); pH 2.7; wet pick up of 100%; drying at 110 °C for min; curing time 90 s.

β-CD in the finishing bath is accompanied by continuous improvement in the wrinkle recovery angle and continuous decrease in the finished fabric's tensile strength and whiteness index, while the fabric's wettability was not greatly affected by increasing the β-CD concentration in the finishing bath. This is due to the esterification reaction between the cotton fabric's hydroxyl groups as well as that of the β-CD and the carboxyl groups of the BTCA through the anhydride intermediate mechanism. The improvement in the wrinkle recovery angle and the decrease in the tensile strength, compared with the corresponding values for the untreated samples declare the role of polycarboxylic acid as a crosslinking agent as is reported in different previous studies (Xiao et al., 2007). The negligible negative effect of β-CD finishing on the fabric's wettability is perhaps due to the hydrophilic nature of β-CD itself, which has large number of hydroxyl groups, and that is why it does not decrease the fabric's wettability by noticeable amount.

3.1.5. Effect of curing temperature on fabric's performance properties

Table 2 shows the performance properties of finished cotton fabrics when carrying out the curing step at different temperatures, namely, 150 °C, 160 °C, 170 °C and 180 °C. All samples were finished using a finishing bath composed of 20% β-CD, 6% BTCA and 1% SHP. All fabrics were padded to wet pick up of 100% and dried at 110 °C for 5 min. It is logic that increasing the curing temperature from 150 °C up to 180 °C for 90 s brings about a significant improvement in the wrinkle recovery angle but this improvement was found to be accompanied with a loss in the fabric's tensile strength and lower value of the whiteness index, while the wettability was not greatly affected by raising the curing temperature. The improvement in the wrinkle recovery angle by raising the curing temperature is due to the enhancement in the crosslinking reaction of cellulose, through esterification with the BTCA. Increasing the curing temperature is logic to improve the fabric's tensile strength, due to enhancement in the crosslinking reaction. On the other hand, curing the fabric at high temperature in acidic medium leads to decrease in the fabric's tensile strength due to the cellulosic chains degradation, by the action of the acidic medium and the high temperature. It is clear from the results that the loss in tensile strength due to cellulosic fibers degradation overcomes the improvement in tensile strength due to the crosslinking reaction and the net result is that the tensile strength decreases by increasing the curing temperature. The lower value of whiteness index compared with the untreated fabric is due to the effect of BTCA which is known to cause yellowness and also due to the β-CD fixation.

3.2. Assessment of antimicrobial activity

Cotton fabrics having antimicrobial activity were prepared by grafting β-CD onto the cotton fabrics through BTCA crosslinking and then the finished fabrics were loaded by the antimicrobial agent OCT. The extent of the antimicrobial activities for the finished cotton fabrics were tested according to the standard Diffusion Disk Method, and the durability of the antimicrobial activity was examined by washing the finished fabrics repeatedly and testing the antimicrobial activity after each washing cycle.

3.2.1. Effect of β-CD finishing on the antimicrobial activity

To show the effect of β-CD finishing on keeping the antimicrobial activity upon repeated washing, a cotton fabric sample finished with β-CD grafting and another unfinished cotton fabric sample were immersed in OCT solution, dried and subjected to only one washing cycles and their antimicrobial activities were tested after such washing cycle. Table 3 shows the inhibition zones of both the finished and unfinished cotton fabrics, against two types of bacteria (Gram positive and Gram negative) as well as two types of fungi. As is clear from Table 3 the inhibition zones for the β-CD finished fabrics are in the range of 7–8.15 mm, while the inhibition zones for the corresponding unfinished fabrics are always zero mm. The antimicrobial activity is measured as mentioned above after one washing cycle. The high value of the inhibition zone for the β-CD-finished cotton fabrics and the zero inhibition zone for the unfinished fabrics, indicate the role of β-CD in hosting the OCT molecules and keeping them enclosed inside the β-CD cavities, such that these molecules are not lost due to the washing process and accordingly, the β-CD-finished cotton fabrics keep their antimicrobial activity even after washing, in contrast to the unfinished cotton fabrics, which was found to lose their antimicrobial activity completely after just one washing.

3.2.2. Effect of amount of fixed β-CD on the antimicrobial activity

To study the effect of the graft yield of the β-CD on the antimicrobial activity of cotton fabrics loaded with OCT, cotton samples finished with β-CD solutions having different concentrations, namely 5%, 10%, 15% and 20% were prepared. Also to show whether the antimicrobial activity comes only from OCT loading or β-CD itself has antimicrobial activity, a control cotton fabric sample was prepared. This control sample was cotton finished with 20% β-CD but not loaded with OCT. the results presented in Table 4 show that the control cotton fabric does not show any antimicrobial activity. This means that neither cotton fabric itself nor the β-CD moiety have any self-antimicrobial activity. In addition, it is clear

Table 3
Antimicrobial activities of β-CD-finished and unfinished cotton fabrics.

Finishing	Inhibition zone (mm)			
	Escherichia coli (G^-)	*Staphylococcus aureus* (G^+)	*Candida albicans* (fungus)	*Aspergillus flavus* (fungus)
β-CD finished fabric	8.15	7.36	7	8.12
Unfinished fabric	0	0	0	0

β-CD, 20%; BTCA, 6% (w/v); SHP, 1% (w/v); pH 2.7; wet pick up of 100%; drying at 110 °C for min; curing temperature, 160 °C; curing time 90 s; OCT, 1%.

Table 4
Antimicrobial activities of cotton fabrics grafted with different amounts of β-CD.

[β-CD] in finishing bath (%)	Inhibition zone (mm)			
	Escherichia coli (G^-)	*Staphylococcus aurous* (G^+)	*Candida albicans* (fungus)	*Aspergillus flavus* (fungus)
5	2.1	2	1.96	2
10	3.9	3.5	3.3	4
15	6.5	6.3	6.1	6
20	8.15	7.36	7	8.12
Control	0	0	0	0

BTCA, 6% (w/v); SHP, 1% (w/v); pH 2.7; wet pick up of 100%; drying at 110 °C for min; curing temperature, 160 °C; curing time 90 s; OCT, 1%.

Table 5
Effect of repeated washing on the antimicrobial activity of cotton grafted with β-CD and loaded with OCT.

Number of washes	Inhibition zone (mm)			
	Escherichia coli (G^-)	*Staphylococcus aureus* (G^+)	*Candida albicans* (fungus)	*Aspergills flavus* (fungus)
0	8.15	7.36	7	8.12
1	8	7	7	8
5	7.7	6.8	6.6	7.9
10	7	6	6	7.2
20	6.5	5.2	5	6.6

β-CD, 20%; BTCA, 6% (w/v); SHP, 1% (w/v); pH 2.7; wet pick up of 100%; drying at 110 °C for 5 min; curing temperature, 160 °C; curing time 90 s; OCT, 1%.

from the results that when cotton fabric samples grafted with β-CD are loaded with the OCT, whatever the graft yield is, the antimicrobial agent is hosted by the cavities of β-CD moieties and the cotton fabrics show good antimicrobial activity, each according to the amount of fixed β-CD. The data presented in Table 4 summarize the antimicrobial activities of different cotton fabric samples having different graft yields (varying amounts of fixed β-CD). According to the increased hosting capacity by increasing the amount of fixed β-CD, it is obvious that increasing the graft yield will be accompanied by an increase in the amounts of OCT incorporated to the β-CD cavities during the immersion in the antimicrobial agent solution and accordingly the antimicrobial activity will increase by increasing the graft yield. This increase in the antimicrobial activity is logic because the hosting capacity toward more guest molecules is dependent on the amount of β-CD fixed onto the cotton fabric.

3.2.3. Effect of repeated washing on cotton fabric's antimicrobial activity

To show the durability of the antimicrobial activity against repeated washing cycles, cotton fabrics grafted with β-CD and loaded with OCT were subjected to a series of repeated washing/drying cycles and the antimicrobial activity is estimated after each washing cycle. The data presented in Table 5 show the repeated washing effect on the durability of the antimicrobial activity for cotton fabrics grafted with β-CD and loaded with OCT. The antimicrobial activity was estimated and its durability was expressed in terms of a factor defined as percent retention. This is estimated according to the inhibition zone of different classes of bacteria and fungi, after each washing cycle. It is noticed from the results in Table 5 that the antimicrobial activity shows decrement upon repeated washing but although this is the situation, the finished cotton fabrics retain a reasonable deal of their antimicrobial activities. This reasonable retention in the antimicrobial activity in spite of repeated washing cycles declares the important role of β-CD in not only hosting the antimicrobial agent molecules, but also making complex with them to keep the antimicrobial agent inside the cavities for longer times, resulting in the noticed long-lasting antimicrobial activity of the β-CD finished cotton fabrics (Wang & Cai, 2008).

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References

Abdel-Halim, E. S. (2012a). An effective redox system for bleaching cotton cellulose. *Carbohydrate Polymers*, *90*, 316–321.
Abdel-Halim, E. S. (2012b). Simple and economic bleaching process for cotton fabric. *Carbohydrate Polymers*, *88*, 1233–1238.
Abdel-Halim, E. S. (2013). Amine salts-activated systems for one-step bleaching of cotton fabrics. *Carbohydrate Polymers*, *96*, 64–70.
Abdel-Halim, E. S., & Al-Deyab, S. S. (2011). Low temperature bleaching of cotton cellulose using peracetic acid. *Carbohydrate Polymers*, *86*, 988–994.
Abdel-Halim, E. S., & Al-Deyab, S. S. (2013). One-step bleaching process for cotton fabrics using activated hydrogen peroxide. *Carbohydrate Polymers*, *92*, 1844–1849.
Abdel-Halim, E. S., Fahmy, H. M., & Fouda, M. M. G. (2008). Bioscouring of linen fabric in comparison with conventional chemical treatment. *Carbohydrate Polymers*, *74*, 707–711.
Abdel-Halim, E. S., Fouda, M. M. G., Hamdy, I., Abdel-Mohdy, F. A., & El-Sawy, S. M. (2010). Incorporation of chlorohexidin diacetate into cotton fabrics grafted with glycidyl methacrylate and cyclodextrin. *Carbohydrate Polymers*, *79*, 47–53.
Abdel-Halim, E. S., Konczewicz, W., Zimniewska, M., Al-Deyab, S. S., & El-Newehy, M. H. (2010). Enhancing hydrophilicity of biosourced flax fabric by emulsification post-treatment. *Carbohydrate Polymers*, *82*, 195–201.
Abdel-Halim, E. S., Abdel-Mohdy, F. A., Al-Deyab, S. S., & El-Newehy, M. H. (2010). Chitosan and monochlorotriazinyl-β-cyclodextrin finishes improve antistatic properties of cotton/polyester blend and polyester fabrics. *Carbohydrate Polymers*, *82*, 202–208.
Abdel-Halim, E. S., Abdel-Mohdy, F. A., Fouda, M. M. G., El-Sawy, S. M., Hamdy, I. A., & Al-Deyab, S. S. (2011). Antimicrobial activity of monochlorotriazinyl-β-cyclodextrin/chlorohexidin diacetate finished cotton fabrics. *Carbohydrate Polymers*, *86*, 1389–1394.
Agrawal, P. B., Nierstrasz, V. A., & Warmoeskerken, M. M. C. G. (2008). Role of mechanical action in low-temperature cotton scouring with *F. solani* pisi cutinase and pectate lyase. *Enzyme and Microbial Technology*, *42*, 473–482.
Arbeitsgruppe. (1987). Textile vorbehandlung. *Melliand Textilberichte*, *8*, 581–583.
Basto, C., Tzanov, T., & Cavaco-Paulo, A. (2007). Combined ultrasound-laccase assisted bleaching of cotton. *Ultrasonics Sonochemistry*, *14*, 350–354.
Baudin, C., Camara, M., & Navaza, A. (2007). Supramolecular crystal structures of per(3,6-anhydro)-α-cyclodextrin grown from KCl or NaI solutions. *Journal of Molecular Structure*, *839*, 58–63.
Buschman, H. J., Denter, U., Knittel, D., & Schollmeyer, E. (1998). The use of cyclodextrins in textile processes—An overview. *Journal of the Textile Institute*, *89*, 554–561.
Buschmann, H. J., Knittel, D., & Schollmeyer, E. (1991). Resin finishing of cotton in the presence of cyclodextrins for depositing fragrances. *Melliand Textilberichte International Textile Reports*, *72*, 198–201.

Del Valle, M. E. M. (2004). Cyclodextrins and their uses. *Process Biochemistry*, *39*, 1033–1036.
Denter, U., Buschmann, H. J., Knittel, D., & Schollmeyer, E. (1997). Modification of fiber surfaces by permanent fixation of supramolecular components. 2. Cyclodextrines. *Angewandte Makromolekulare Chemie*, *248*, 165–188.
Desmet, G., Takács, E., Wojnárovits, L., & Borsa, J. (2011). Cellulose functionalization via high-energy irradiation-initiated grafting of glycidyl methacrylate and cyclodextrin immobilization. *Radiation Physics and Chemistry*, *80*, 1358–1362.
Dodziuk, H. (2006). *Cyclodextrins and their complexes: Chemistry, analytical methods, applications*. Weinheim: Wiley-VCH Verlag GmbH.
Dogan, A. A., Adiloglu, A. K., Onal, S., Cetin, E. S., Polat, E., Uskun, E., et al. (2008). Short-term relative antibacterial effect of octenidine dihydrochloride on the oral microflora in orthodontically treated patients. *International Journal of Infectious Diseases*, *12*, 19–25.
Fahmy, H. M., & Abdel-Halim, E. S. (2010). Utilization of poly (N-vinyl-2-pyrrolidone) to enhance the performance and antibacterial properties as well as UV protection of ester crosslinked cotton fabrics. *Journal of Industrial Textiles*, *40*, 109–121.
Ghosh, A., Biswas, S., & Ghosh, T. (2011). Preparation and evaluation of silymarin β-cyclodextrin molecular inclusion complexes. *Journal of Young Pharmacists*, *3*, 205–210.
Irob, O. N., Young, M. M., & Apderson, W. A. (1996). Antimicrobial activity of annato extract. *International Journal of Pharmacology*, *34*, 87–90.
Ishiwata, S., & Kamiya, M. (1999). Cyclodextrin inclusion: Catalytic effects on the degradation of organophosphorus pesticides in neutral aqueous solution. *Chemosphere*, *39*, 1595–1600.
Kramer, A., & Assadian, O. (2013). SP19-4 octenidine dihydrochloride—Characteristics and clinical use. *International Journal of Antimicrobial Agents*, *42*, 21–23.
Krishna, B. V. S., & Gibb, A. P. (2010). Use of octenidine dihydrochloride in meticillin-resistant *Staphylococcus aureus* decolonisation regimens: A literature review. *Journal of Hospital Infection*, *74*, 199–203.
Li, N., & Xu, L. (2010). Thermal analysis of β-cyclodextrin/berberine chloride inclusion compounds. *Thermochimica Acta*, *499*, 166–170.
Medronho, B., Andrade, R., Vivod, V., Ostlund, A., Miguel, M. G., Lindman, B., et al. (2013). Cyclodextrin-grafted cellulose: Physico-chemical characterization. *Carbohydrate Polymers*, *93*, 324–330.
Mistik, S. I., & Yükseloglu, S. M. (2005). Hydrogen peroxide bleaching of cotton in ultrasonic energy. *Ultrasonics*, *43*, 811–814.
Mohsin, M., Rasheed, A., Farooq, A., Ashraf, M., & Shah, A. (2013). Environment friendly finishing of sulphur, vat, direct and reactive dyed cotton fabric. *Journal of Cleaner Production*, *53*, 341–347.
Murthy, C. N., & Shown, I. (2009). Grafting of cotton fiber by water-soluble cyclodextrin-based polymer. *Journal of Applied Polymer Science*, *111*, 2056–2061.
Nguyen, T. A., Liu, B., Zhao, J., Thomas, D. S., & Hook, J. M. (2013). An investigation into the supramolecular structure, solubility, stability and antioxidant activity of rutin/cyclodextrin inclusion complex. *Food Chemistry*, *136*, 186–192.
Ouziel, P., & Kulke, T. (2007). *United States Patent No. 20070277328*.
Pedersen, M., Bjerregaard, S., Jacobsen, J., & Sørensen, A. M. (1998). A genuine clotrimazole γ-cyclodextrin inclusion complex-isolation, antimycotic activity, toxicity and an unusual dissolution rate. *International Journal of Pharmaceutics*, *176*, 121–131.
Peng, S., Gao, Z., Sun, J., Yao, L., & Qiu, Y. (2009). Influence of argon/oxygen atmospheric dielectric barrier discharge treatment on desizing and scouring of poly (vinyl alcohol) on cotton fabrics. *Applied Surface Science*, *255*, 9458–9462.
Puliti, R., Mattia, C. A., & Paduano, L. (1998). Crystal structure of a new α-cyclodextrin hydrate form. Molecular geometry and packing features: Disordered solvent contribution. *Carbohydrate Research*, *310*, 1–8.
Savarino, P., Viscardi, G., Quagliotto, P., Montoneri, E., & Barni, E. (1999). Reactivity and effects of cyclodextrins in textile dyeing. *Dyes and Pigments*, *42*, 143–147.
Scalia, S., Tursilli, R., Bianchi, A., Nostro, P. L., Bocci, E., Ridi, F., et al. (2006). Incorporation of the sunscreen agent, octyl methoxycinnamate in a cellulosic fabric grafted with β-cyclodextrin. *International Journal of Pharmaceutics*, *308*, 155–159.
Shao, Y., Martel, B., Morcellet, M., Weltrowski, M., & Crini, G. (1996). Sorption of textile dyes on β-cyclodextrin–epichlorhydrin gels. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, *25*, 209–212.
Stahl, J., Braun, M., Siebert, J., & Kietzmann, M. (2010). The effect of a combination of 0.1% octenidine dihydrochloride and 2% 2-phenoxyethanol (octenisept®) on wound healing in pigs in vivo and its in vitro percutaneous permeation through intact and barrier disrupted porcine skin. *International Wound Journal*, *7*, 62–69.
Szejtli, J. (1988). *Cyclodextrin technology*. Dordrecht: Kluwer Academic Publishers.
Szejtli, J. (2003). Cyclodextrins in the textile industry. *Starch-Starke*, *55*, 191–196.
Tanapongpipat, A., Khamman, C., Pruksathorm, K., & Hunsom, M. (2008). Process modification in the scouring process of textile industry. *Journal of Cleaner Production*, *16*, 152–158.
Teli, M. D., Sheikh, J., & Bhavsar, P. (2013). Multifunctional finishing of cotton using chitosan extracted from bio-waste. *International Journal of Biological Macromolecules*, *54*, 125–130.
Tian, L., Branford-White, C., Wang, W., Nie, H., & Zhu, L. (2012). Laccase-mediated system pretreatment to enhance the effect of hydrogen peroxide bleaching of cotton fabric. *International Journal of Biological Macromolecules*, *50*, 782–787.
Veiga, M. D., & Ahsan, F. (2000). Influence of surfactants (present in the dissolution media) on the release behaviour of tolbutamide from its inclusion complex with β-cyclodextrin. *European Journal of Pharmaceutical Sciences*, *9*, 291–299.
Vismara, E., Melone, L., Gastaldi, G., Cosentino, C., & Torri, G. (2009). Surface functionalization of cotton cellulose with glycidyl methacrylate and its application for the adsorption of aromatic pollutants from wastewaters. *Journal of Hazardous Materials*, *170*, 798–808.
Voncina, B., & Le Marechal, A. M. (2005). Grafting of cotton with beta-cyclodextrin via poly(carboxylic acid). *Journal of Applied Polymer Science*, *96*, 1323–1328.
Voncina, B., & Majcen, N. (2004). Application of cyclodextrin for medical and hygienic textiles. *Tekstil*, *53*, 1–9.
Wang, J., & Cai, Z. (2008). Incorporation of the antibacterial agent, miconazole nitrate into cellulosic fabric grafted with β-cyclodextrin. *Carbohydrate Polymers*, *72*, 695–700.
Wang, C. X., & Chen, Sh. L. (2006). Surface treatment of cotton using β-cyclodextrins sol–gel method. *Applied Surface Science*, *252*, 6348–6352.
Wang, J., Cao, Y., Sun, B., & Wang, C. (2011). Characterisation of inclusion complex of trans-ferulic acid and hydroxypropyl-β-cyclodextrin. *Food Chemistry*, *124*, 1069–1075.
Xiao, J., Zhang, S., Yang, J., & Huang, Q. (2007). Study on chemical bonding of polycarboxylic acid black on cotton and its dyeing and finishing properties. *Dyes and Pigments*, *73*, 111–117.
Yamamoto, S., Kurihara, H., Mutoh, T., Xing, X. H., & Unno, H. (2005). Cholesterol recovery from inclusion complex of β-cyclodextrin and cholesterol by aeration at elevated temperatures. *Biochemical Engineering Journal*, *22*, 197–205.
Yang, H., & Yang, C. Q. (2005). Durable flame retardant finishing of the nylon/cotton blend fabric using a hydroxyl-functional organophosphorus oligomer. *Polymer Degradation and Stability*, *88*, 363–370.