Carbohydrate Polymers 88 (2012) 950–958

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Modification of β-cyclodextrin with itaconic acid and application of the new derivative to cotton fabrics

Malihe Nazi [a], Reza Mohammad Ali Malek [a,*], Richard Kotek [b]

[a] Textile Engineering Department, Amirkabir University of Technology, 424 Hafez Ave, 15875-4413 Tehran, Iran
[b] College of Textiles, North Carolina State University, Raleigh, NC 27695, USA

ARTICLE INFO

Article history:
Received 2 December 2011
Received in revised form 12 January 2012
Accepted 16 January 2012
Available online 24 January 2012

Keywords:
β-Cyclodextrin itaconate
Cotton fabrics
Esterification
Graft copolymerisation

ABSTRACT

β-Cyclodextrin (β-CD) is capable of forming inclusion complexes but cannot form a direct covalent bond with textile materials; hence, some cyclodextrin derivatives have been synthesised with reactive groups to allow them to chemically bind to various substrates. In this study, β-CD was modified with itaconic acid containing carboxyl and vinyl groups because this bifunctional compound can be attached to β-CD via the esterification reaction and because its vinyl group can perform free-radical polymerisation. The synthesised cyclodextrin itaconate was characterised using elemental and thermal analyses, solubility testing and NMR, FTIR and Raman spectroscopy. In addition, the impact of the grafting of this vinyl monomer on the performance of cotton fabric was investigated. The presence of anchored CD nanoparticles on the surface of the fibres was demonstrated by using SEM and FTIR as well as the ability of the attached CDs to form inclusion complexes.

1. Introduction

Cyclodextrins (CDs) are macrocyclic compounds composed of six to eight ($\alpha = 6$, $\beta = 7$, $\gamma = 8$) D-Glucose units linked together by α-(1,4)-glycosidic bonds (Freudenberg & Cramer, 1948; Vögtle, 1991), which can be obtained from the degradation of starch with a glucosyltransferase enzyme (Croft & Bartsch, 1983; Sanger, 1980). In CDs, each glucopyranose unit contains three free hydroxyl groups, which differ both in their availability and reactivity. Primary and secondary hydroxyl groups in CDs are located on the lower and upper ridges of the torus-shaped cavity (Dodziuk, 2006; Szejtli, 1988). In addition, the molecule's glycosidic oxygen atoms provide an electron-rich environment in the interior of the cavity (Ouziel & Kulke, 2007). Thus, due to the hydrophilic exterior and hydrophobic interior of these compounds (Dodziuk, 2006; Szejtli, 1988), CDs can incorporate a variety of hydrophobic compounds in their cavities, via host-guest complexation (Shao, Martel, Morcellet, Weltrowski, & Crini, 1996; Szejtli, 1982, 1996). Therefore because of the molecular encapsulation property of CDs, they are used in cosmetics (Wang & Chen, 2005), pharmaceuticals (Loftsson & Masson, 2001; Tabushi, 1982), chemicals (Szejtli, 1998), chromatography (Misiuk & Zalewska, 2008), textile dyeing and finishing (Buschmann, Knittel, & Schollmeyer, 2001; Cireli & Yurdakul, 2006; Kumbasar, Atav, & Yurdakul, 2007; Savarino, Viscardi, Quagliotto, Montoneri, & Barni, 1999; Shibusawa, Okamoto, Abe, & Sakata, 1998; Szejtli, 2003; Voncina, Vivod, & Jausovec, 2007), foods and several other industries (Del Valle, 2004).

In addition, a large number of cyclodextrin derivatives and their preparation processes have recently been introduced with compounds capable of reacting with their hydroxyl groups (Dodziuk, 2006; Ouziel & Kulke, 2007; Szejtli, 1997; Yoshinaga, 1992). Amongst these derivatives, reactive cyclodextrins have also been applied in textile industries (Buschmann et al., 2001; Otta, Zsadon, Farago, Szejtli, & Tudos, 1988; Schmidt, Buschmann, Knittel, & Schollmeyer, 2005) because natural or synthetic polymers containing nucleophilic groups can react with these derivatives by forming a covalent bond (Buschmann, Deuter, Knittel, & Schollmeyer, 1988; Denter & Schollmeyer, 1996; Gaffar, El-Rafie, & El-Tahlawy, 2004; Lee, Yoon, & Ko, 2000; Pöpping & Deratani, 1992; Reuscher & Hinsenkorn, 1996; Reuscher, Hirsenkorn, & Haas, 1998; Szejtli, 2003). However, it seems that these compounds have both advantages and disadvantages. For example, monochlorotriazinyl-β-cyclodextrin (CDMCT), which is a commercially reactive cyclodextrin derivative, is usually able to bond to membranes, foils, films, textiles, leather, and chromatographic separation phases, amongst others (Denter & Schollmeyer, 1996; Reuscher & Hinsenkorn, 1996; Reuscher et al., 1998; Schmidt et al., 2005). However, achieving accessibility to the cavities of all of the fixed cyclodextrin molecules is not easy (Grechin, Buschmann, & Schollmeyer, 2007; Schmidt et al., 2005). Hence, there is currently an increasing demand for improved reactive CD derivatives with better stability after storage under different conditions and

* Corresponding author. Tel.: +98 2164542662; fax: +98 2164542600.
E-mail address: rmamalek@aut.ac.ir (R.M.A. Malek).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2012.01.047

processes without cleavage or the production of toxic or harmful subsidiary products. Furthermore, it would be preferable for the derivatives to not be comprised of complicated mixtures of variously substituted cyclodextrin derivatives and their isomers (Ouziel & Kulke, 2007).

To achieve this goal, in this study, a reactive derivative is provided in which the β-cyclodextrin was modified with a bifunctional compound containing carboxyl and vinyl groups via the esterification reaction. For this purpose, itaconic acid (IA) was chosen because it is used worldwide to create useful polyfunctional building blocks in different biomedical fields, such as drug delivery systems (Okabe, Lies, Kanamasa, & Park, 2009). The structural information of synthesised cyclodextrin itaconate was characterised, and the grafting copolymerisation of this reactive cyclodextrin on cotton fabric was studied. The presence of bounded CDI and its ability for molecular encapsulation were investigated by using SEM, measuring decreases in the absorbance intensity of phenolphthalein and the inclusion complex formation of cyclohexane.

2. Materials and methods

2.1. Materials

β-Cyclodextrin (β-CD) and ceric ammonium nitrate (CAN) were supplied by Sigma Aldrich Co. and used as received without further purification. Itaconic acid (IA) was supplied by Fluka Co., and sodium hypophosphite (SHP) was used as a catalyst as a laboratory grade chemical. The fabric (96 g/m^2) was 100% cotton scoured, desized, and bleached printcloth.

2.2. Preparation of β-cyclodextrin itaconate (CDI)

CDI was prepared by reacting β-CD (1 mol/L) with itaconic acid (2.6 mol/L) in the presence of sodium hypophosphite (0.33 mol/L) as a curing catalyst in a semi-dry medium with a material to liquor ratio of 1:1.15, at 110 °C for 115 min in a circulating air oven. The cured sample was purified twice by washing with 200 mL of isopropyl alcohol and filtered with the suction filtration method to remove unreacted ingredients, followed by drying at 60 °C for 24 h. In our previous work, by applying the response surface methodology (RSM), the interactive effects of parameters affecting the reaction mechanisms were investigated, and this optimum conditions for synthesis of this product were determined by controlling the reaction mechanisms (Nazi, Malek, & Moghaddam, 2010). The yield of CDI under these conditions was 84% based on β-CD. Additionally, as an absolutely purified sample is essential for characterisation, the sample was further purified to completely separate the unreacted β-CD from the CDI. For this purpose, deionised water was added slowly and carefully to the sample with stirring to achieve complete dissolution. Then isopropyl alcohol was added slowly and carefully to the solution with slow stirring until the solution was cloudy. The CDI precipitated due to its insolubility in isopropyl alcohol and was then separated by centrifugation.

Because in this work we proposed to produce reactive cyclodextrin containing vinyl functional groups for applying to modify cotton fabric, the ability of CDI for free-radical homopolymerisation was investigated. The solutions containing CDI were warmed until complete dissolution occurred and then cooled down to room temperature. Ceric ammonium nitrate (CAN) (0.015 mol/L) and nitric acid (1%) were added to the solution to initiate polymerisation, and the sample was kept at 30 °C for 24 h in a closed tube with stirring. The solution was then cast onto Teflon sheets. The films were allowed to dry at 25 °C for at least 24 h and then spread uniformly over the sheets using acetone solution. These polymerised cyclodextrin itaconate (PCDI) films were then dried and stored at room temperature.

2.3. Modification of cotton fabric with cyclodextrin itaconate

In this study, CAN was applied to generate free radicals on the surface of the fabrics. As previously reported, the consumption rate of Ce (IV) is much higher in the case of CDI compared with β-CD (Gaffar et al., 2004), and because the equilibrium complex formation constant of β-CD for Ce (IV) is lower than that of cellulose (Lee et al., 2000), it seems that the initial Ce (IV) consumption rate of CDI might be much higher than that of cellulose. Therefore, the formation of free radicals on the cellulose chain backbone, occurring before treatment with CDI, was thought to be advantageous for grafting.

To investigate the method of graft copolymerisation on cotton, three approaches were followed. In pad-thermofixation and semi-continuous pad-batch methods, the samples were immersed in a 1% nitric acid solution containing (0.016 mol/L) CAN as the initiator, padded twice for a wet pickup of 100% and then dried at room temperature with air circulation for 5 min. These pre-treated samples were immediately employed for the next step, impregnated in a solution containing 20 g/L CDI and padded twice through squeeze rollers (pick up of 100%). In pad-thermofixation method, the sample was dried at 80 °C for 2.5 min and cured at 165 °C for 1 min and in semi-continuous pad-batch method the sample was stored in a plastic bag for 3 h. In a batch system, the sample was placed in an aqueous 1% nitric acid solution containing (0.016 mol/L) CAN at 30 °C for 30 min, followed by the addition of 100 g/L CDI. Then the formation of graft copolymers on the cellulose chain backbone took place at 50 °C after 2 h. The unreacted chemicals and homopolymers were removed from the sample by extensive washing with hot and cold deionised water. The treated fabrics were then dried at 100 °C for 2 h and weighted.

To evaluate the effect of reaction parameters on the performance of the modified fabrics, the samples were pre-treated with CAN (0–0.015 mol/L), padded with CDI (10–50 g/L), then dried at different temperatures (60–100 °C) for various times (1–5 min), and finally cured at the temperature between 120 and 210 °C for a length of time about 0.5–5 min in the pad-thermofixation method.

2.4. Characterisation and evaluation techniques

To determine the solubility of β-CD and its synthesised derivative, an adaptation of the method proposed by Jozwiakowski and Connors (1985) was used. Excess amounts of each sample were placed in vials with 10 mL of deionised water. The samples were agitated by rotation in a constant-temperature bath at 25 °C until equilibrium was reached (for 10 h). The excess solid phase was separated from the solution phase by means of a filtration system. The samples were placed in a 110 °C oven for 3 h and weighed to within ±0.0001 g.

Elemental analysis testing was carried out with an Elementar Analysen System GmbH: vario MAX CN automatic instrument. The samples were kept under ambient conditions of 25 °C and 40% RH for 24 h before measuring.

Thermogravimetric analysis (TGA) measurements were performed using a Perkin Elmer thermogravimetric analysis device. Weight rate changes versus temperature were evaluated whilst the samples were heated from 20 to 600 °C at a rate of 10 °C/min.

Thermal analysis testing was conducted using a TA Instruments DSC Model 2010 differential scanning calorimeter. Because thermal decomposition of β-CD occurs at about 250 °C (Szejtli, 1988), each sample was scanned at a rate of 10 °C/min over a range of 25–200 °C under a nitrogen flow.

^{1}H and ^{13}C NMR spectra were collected on a Bruker Avance 500-MHz NMR spectrometer. Samples were run in dimethyl sulfoxide (DMSO) with an ambient probe temperature.

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS 670 spectrophotometer at a resolution of 4 cm^{-1} over a range of 400–4000 cm^{-1}. The KBr disc method was used for powder samples. ATR was applied for fabrics.

Raman spectra were recorded from 100 to 4200 cm^{-1} on a Fourier transform Almega Thermo Nicolet dispersive Raman spectrometer with a resolution of 4 cm^{-1}.

The grafting rate was determined by the weight increase according to the following equation:

$$\text{Graft yield}\,(\%) = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 are the weights of the dry fabric sample before and after grafting, respectively.

Tensile strength testing was carried out using an Instron Universal testing machine, ASTM D-5035. The tensile strength loss was calculated according to the following equation:

$$\text{Tensile strength loss}\,(\%) = \frac{TS_1 - TS_2}{TS_1} \times 100$$

where TS_1 and TS_2 are the tensile strength of the control and modified fabrics, respectively.

The wrinkle recovery angle (WRA) was measured according to AATCC standard method 66–1996 and any changes in the wrinkle recovery angle were calculated by the following equation:

$$\text{Relative WRA}\,(\%) = \frac{WRA_1 - WRA_2}{WRA_1} \times 100$$

where WRA_1 and WRA_2 are the wrinkle recovery angles of the control and modified fabrics, respectively.

Field emission scanning electron microscopy (FE-SEM) analysis of the control and modified fabrics was performed using a Hitachi model S4160 FE-SEM with a Technics Hummer II sputter coater.

The presence of CDI was shown by the ability of phenolphthalein to form inclusion complexes with β-CD and its derivatives (in alkaline solutions, pH ca. 11) based on complex formation causing a decrease in the absorption of light (Goel & Nene, 1995). For this purpose, a specific weight of the fabric was immersed in phenolphthalein solution, and after 2 h, the absorbance intensity of the solution at 550 nm was determined using a Cary 300 UV-Visible spectrophotometer. The decrease in absorbance intensity was calculated according to the following equation:

$$\text{Decrease in absorbance intensity}\,(\%) = \frac{\text{control} - \text{test}}{\text{control}} \times 100$$

where the control and test variables are the absorbance intensity of the solutions containing control and modified fabrics, respectively.

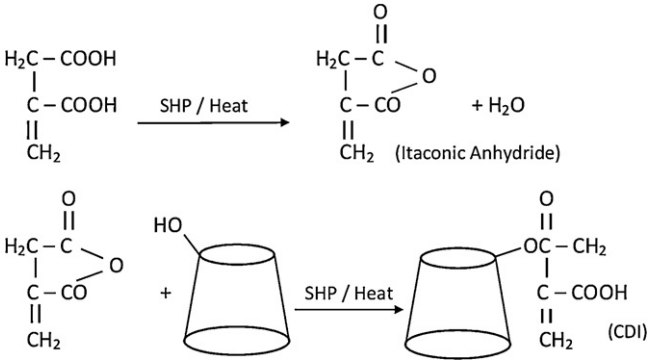
To investigate the inclusion compound formation on the surface of the modified fabric, samples were treated with cyclohexane in a vacuum desiccator for 48 h at room temperature. Because cyclohexane is a hydrophobic compound and evaporates easily at room temperature, evaporated cyclohexane molecules can be entrapped in the cavity of CDs on the surface of modified fabric. The hydrophobicity of the surface was determined by measuring the contact angle using an optical contact angle measuring instrument (OCA20).

3. Results and discussion

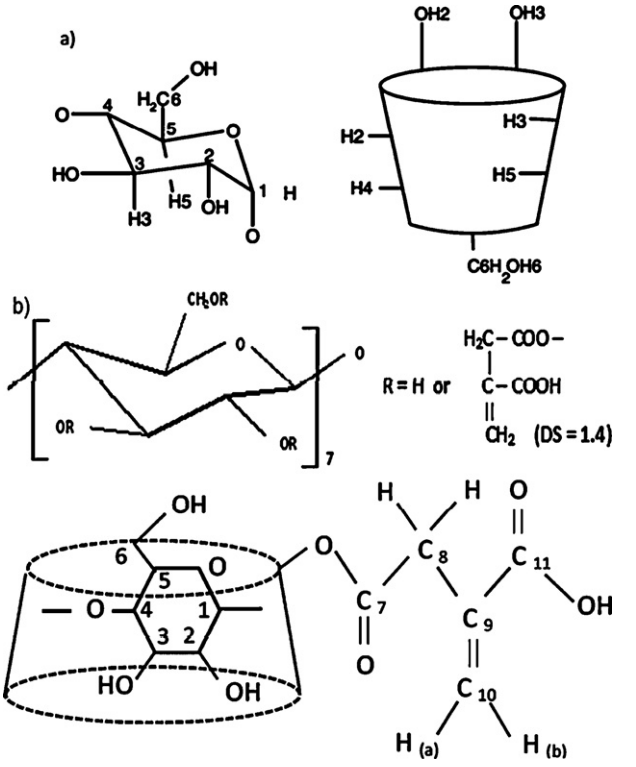
3.1. Preparation of β-cyclodextrin itaconate (CDI)

3.1.1. Tentative mechanism

Chemically reactive cyclodextrin was prepared via the reaction of β-CD with itaconic acid to obtain vinyl monomers. IA is a bifunctional monomer that has carboxylic groups capable of modifying β-CD by the esterification reaction and a vinyl group capable of undergoing polymerisation, depending on the reaction conditions used. As suggested by other researchers (Gaffar et al., 2004; Yang & Wang, 1996), the esterification of β-CD by IA in the presence of a catalyst can be explained according to the cyclic anhydride reactive intermediate mechanism (Scheme 1).



Scheme 1. The probable esterification reaction of β-CD with IA.



Scheme 2. Schematic view of (a) the glucopyranoside ring with the atom numbering and the average orientation of the most important atoms and OH groups in CDs and (b) molecular structure of CDI (or RCD) and the atom numbering of cone-shaped CDI covered with one D-glucose subunit and itaconate component.

3.1.2. Solubility studies

The solubility results in water at 25 °C showed that the solubility of CDI (30.39 g/L) is clearly higher than that of β-CD (18.51 g/L). However, after polymerisation, the solubility decreased to 14.31 g/L.

It is well known that amongst three kinds of hydroxyl groups of β-CD (Scheme 2b), electrophilic reagents initially attack C_6-OH groups (Dodziuk, 2006), and also, due to the strong intramolecular hydrogen bonds formed on the wide side of cavity, the

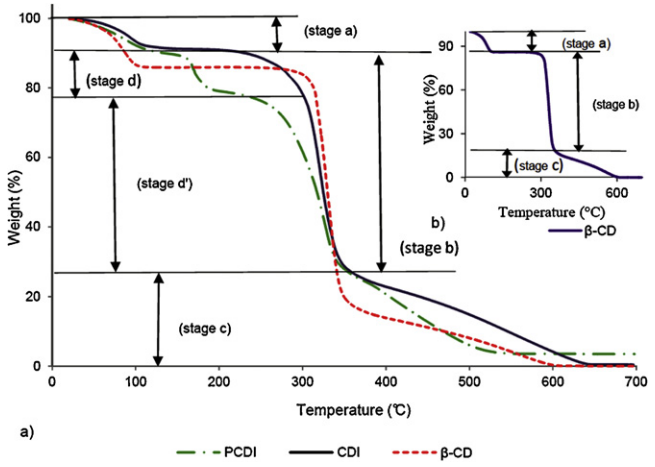


Fig. 1. (a) TGA curves of PCDI, CDI and β-CD and the stages of weight loss process for CDI and PCDI and (b) TGA curve of β-CD and three stages of its weight loss process.

probability of itaconic acid reaction with the flexible C_6-OH groups is higher than the other hydroxyl groups (Scheme 2b). Moreover, the presence of the new carboxylic groups allows for a favourable local accommodation of H_2O molecules around the CDI molecules, resulting in their higher solubility in comparison to β-CD. However, as expected, the solubility of CDI after polymerisation (PCDI) decreases due to its higher molecular weight.

3.1.3. Elemental analysis

The elemental analysis results indicated that the carbon and hydrogen contents in β-CD were 39.1% and 6.7%, respectively, whilst they were 40.6% and 6.5% for CDI, respectively. As mentioned in the literatures, the number of water molecules inside and outside of the cavity in β-CD ($C_{42}H_{70}O_{35}$) is about 8–12 molecules (Bilal, de Brauer, Claudy, Germain, & Létoffé, 1995; Raffaini & Ganazzoli, 2007; Szejtli, 1988) so it seems that it is approximately eight under ambient conditions. Thus, it can be assumed that the number of water molecules bound to one CDI molecule is the same as that of a β-CD molecule. Therefore, the degree of substitution (DS) for this reaction seems to be 0.2 per anhydroglucose or 1.4 itaconate substitutions per CD molecule.

3.1.4. Thermal analysis

The DSC curve of CDI showed an endothermic effect initiating at approximately 25 °C, demonstrating that the mass loss of water molecules in CDI took place at the same temperature for β-CD in the hydrate state (Song et al., 2008; Szejtli, 1988). Water liberation, which was observed around 104 °C for β-CD, occurred at about 85 °C for CDI. The results also indicate that the release enthalpy of water molecules for CDI (162 J/g) is clearly lower than that of β-CD (314 J/g). Therefore, it seems that the energy of the interactions between the CD molecules of CDI in the solid state and the water molecules as well as the probability distribution of the water molecules may be different from β-CD.

Fig. 1 illustrates the thermogravimetric examination results for β-CD, CDI and PCDI. According to the TGA curves (β-CD (Fig. 1b); CDI and PCDI (Fig. 1a)), their weight loss processes can be divided into three stages. The decomposition temperature (*T*) corresponding to a rapid weight loss, the temperature range (TR), the weight loss (WL) at each stage of the thermal decomposition of β-CD, CDI and PCDI, and the residual loss (RL) at 355.6 °C are presented in Table 1. The first weight loss (stage a) in the temperature range of 25–150 °C (Table 1) can be attributed to the release of water molecules, including complexed water inside and non-complexed water outside the cavity. The second weight loss (stage b) in the temperature range of about 210–355 °C (Table 1) is due to decomposition of the main structure. Finally, a nonlinear decline of the remnants appeared (stage c), corresponding to slow carbonisation and incineration. It can easily be observed from Fig. 1a that stage b of PCDI can be divided into two stages (d, d′) and that a new stage appeared in the process of its thermal decomposition.

It is clear that there is a conceptual difference between the thermal decomposition behaviours of these compounds. The onset temperatures of the cyclic structure degradation of the β-CD, CDI and PCDI samples were 314.56, 298.73 (stage b) and 290.18 °C (stage d′), respectively. Therefore, as there was not much difference in the temperatures of the degradation onset, it seems that the cyclic structure degradation (Szejtli, 1988) of the different samples proceeded in a similar manner. However, due to decomposition of the attached itaconate groups in CDI and PCDI, the molecule degradation occurred at a lower temperature (about 212 °C in stages b and d′). Furthermore, regarding the PCDI degradation, the weight loss in stage d (occurring around 146–212 °C) was approximately 11 wt.% (Table 1); therefore, according to our calculations (M $C_5H_4O_3$ = 112 g/mol), it seems that this decomposition might be related to the degradation of polymerised itaconate groups. Thus, these results demonstrate a decrease in the thermal stability of CD after reacting with itaconic acid.

3.1.5. NMR analysis

In this study, NMR spectroscopy with a magnetic field 500 MHz was used for characterisation of the itaconate cyclodextrin. As the interaction between DMSO (used as a solvent) and hydroxylated molecules through hydrogen bonding can affect the conformation and reactivity of CDs (Schneider, Hacket, & Rüdiger, 1998), the resolved signals for hydroxyl protons were closely examined.

According to ^{1}H NMR, the proton signals of the anhydroglucose units in CDI exhibited values similar to those of β-CD (Schneider et al., 1998; Szejtli, 1988). Thus, it seems that there are no changes in the CDI cyclic structure. Although, the OH-6 proton in CDI, in comparison with β-CD (Schneider et al., 1998), exhibited no chemical shift, it showed a decrease in the width of the band, where its signal appeared as a singlet in CDI instead of the triplet in β-CD. Thus, in accordance with the difference in the OH-6 proton coupling constant, it is expected that the esterification reaction between β-CD and itaconic acid on the narrow side of cavity is more probable than on the wider side.

^{1}H NMR spectra of CDI showed that =CH_2 resonances in the itaconate group ($H_{(a)}$-10 and $H_{(b)}$-10 in Scheme 2b) clearly occurred as two singlets at different chemical shifts of 5.7 and 6.1 ppm. In addition, due to interference between the carboxymethyl groups' proton signals (around 3.3 ppm) and the signals of anhydroglucose units, the complete separation of these signals was difficult. It should be noted that the integration of NMR spectra indicates a degree of substitution values (DS = 1.4) calculated by this method and confirms the earlier calculations based on other measurements.

^{13}C NMR shifts extend over a much larger scale than proton shifts and are particularly suited to identifying cyclodextrins. The ^{13}C NMR spectrum of CDI in comparison with that of β-CD (Schneider et al., 1998; Szejtli, 1988) was essential in confirming carboxymethylation, as a diagnostic peak arising from the carboxylic carbon (C-11 in Scheme 2b) was observed around 172 ppm. A new peak observed at 112 ppm might correspond to the ethylene carbon (=CH_2) in the itaconate group of CDI. Moreover, peaks attributed to the methylene group (CH_2) overlapped with multiple peaks of the solvent around 40.6 ppm. Furthermore, this spectrum did not show any additional peaks for C-9 or C-7 of the carboxylate group in the itaconate component, as signals from quaternary carbons (C-9) and carbon without attached protons (C-7) had a very low relative intensity.

Table 1
Thermal decomposition process of β-CD, CDI and PCDI.

Compound	Stage a				Stage b			Stage c
	WL (%)	T (°C)	n H_2O	TR (°C)	WL (%)	T (°C)	TR (°C)	RL (%)
β-CD	14.11	86.11	10.36	25–150	66.90	330.22	282.52–355.60	18.27
CDI	8.72	94.12	6.86	25–150	63.11	321.88	212.37–355.59	27.62

Compound	Stage a				Stage d	Stage d′	Stage d	Stage d′	Stage d	Stage d′	Stage c
	WL (%)	T (°C)	n H_2O	TR (°C)	WL (%)		T (°C)		TR (°C)		RL (%)
PCDI	10.53	88.96	8.44	25–150	10.96	51.74	169.02	326.74	146.84–212.63	212.63–355.64	26.92

T: decomposition temperature with a rapid weight loss, TR: temperature range, WL: weight loss and RL: residual loss.

3.1.6. FTIR and Raman analysis

Infrared and Raman spectroscopy are commonly used to identify the chemical structure of synthesised CD derivatives. Thus, the infrared and Raman spectra of the cyclodextrin itaconate were obtained and compared with those of β-cyclodextrin, as shown in Fig. 2a and b. The chemical structure of CDI can also be clearly recognised after polymerisation (PCDI spectra in Fig. 2a) in the FTIR spectrum.

According to the FTIR spectra (Fig. 2a), the OH stretching vibration band of β-CD in the range of 3600–2800 cm^{-1} was broad up to lower frequencies of 2400 cm^{-1} in CDI and PCDI due to the presence of the itaconate carboxylic groups. It can be clearly observed that the wide OH deformation vibration band of the β-CD's hydroxyl group located at 1750–1590 cm^{-1}, the intense band at 1640 cm^{-1}, and the C=O stretching of the carboxylic group and the C=C stretching vibration present in IA at 1704 and 1628 cm^{-1}, respectively might overlap with the C=O stretching vibration band attributed to the esteric carboxylic group of CDI, leading to peaks located at 1643 and 1720 cm^{-1}. However, the C=O stretching band of the carboxylic group and the OH deformation vibration of CD were split into two peaks at 1710 and 1637 cm^{-1} in PCDI, as the relative absorbance band related to the C=C group had disappeared from this region.

Similar overlapping trends were observed in the Raman spectra (Fig. 2b) in the range of 1840–1600 cm^{-1}. Additional peaks with weak bands at 1680, 3120, and 1727 cm^{-1} corresponding to C=C stretching, asymmetric $=CH_2$ stretching of vinyl and C=O stretching vibrations, respectively, indicate the presence of a double bond and ester carbonyl groups in CDI.

3.2. Application of CDI to cotton fabric

3.2.1. Cotton fabric modified with CDI

The results show that graft yields of the fabrics modified with CDI were very low. It seems that the low reaction rate may be associated with the steric resistance of the CD groups. In addition, because CDs have a much larger molecular size than other vinyl monomers (Lee et al., 2000), when passing through small cellulose microfibril pores (Hajny & Reese, 1969; Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998), their penetration into the amorphous region of the cellulose is less probable. Thus, grafting of CDI may occur on the surface of the fabric. Moreover, based on the low graft yield obtained for the three different procedures for surface modification, it seems that in the pad-thermofixation and pad-batch procedures, due to the limited number of monomers on the surface, there were partial monomer aggregations capable of in situ CDI polymerisation and anchoring to cellulosic chains. Additionally, in the batch process, because of CDI's ability for homopolymerisation and in accordance with the characterisation results of PCDI, it can be assumed that the monomers preferentially homopolymerise in solution instead of bonding to cellulose.

The characterisation results of the fabrics modified by different processes are summarised in Table 2, together with the results of the control fabric and a sample treated with CAN according to the pad thermofixation method without the application of CDI. It was found that, despite a reduction in the mechanical strength and wrinkling ability due to the oxidation of CAN, graft copolymerisation of CDI can improve the performance of the samples. In addition, the results of the absorbance intensity of phenolphthalein solution at 550 nm show the presence of CDI on the modified cotton surface due to the formation of phenolphthalein inclusion complexes in the cavity of the CD. Therefore, despite the low graft yields, the characterisation results of the modified fabrics suggest that the application of CDI via these procedures can improve the performance of cotton fabrics.

3.2.2. ATR-FTIR of modified fabric

The reaction of CDI with cellulose was confirmed by comparing the ATR-FTIR spectra of the control fabric and the fabric modified with CDI, as shown in Fig. 2c. The spectrum of the fabric modified with CDI showed a broad band at 2919 cm^{-1}, corresponding to the symmetric $-CH_2$ stretching vibration of CDI. Moreover, the appearance of an additional peak at 1736 cm^{-1} can be attributed to the C=O stretching vibration of the carboxylic groups due to cellulose oxide degradation and or the esterification reaction between CDI and the cellulose.

3.2.3. Tentative mechanisms

It would be helpful to consider the probable modification mechanisms of cotton (Scheme 3) with CDI under the influence of CAN used as the catalyst to induce free-radical polymerisation and graft copolymerisation of CDI on cellulose. These reactions would be expected to eventually occur via changes in the chemical and physical nature of cotton during the overall process. The graft copolymerisation of CDI on the cellulose may occur after the oxidation of cellulose by Ce (IV) (El-Alfy, Khalil, & Hebeish, 1981; Pottenger & Johnson, 1970), as shown in Eq. (1(a)). Free radicals of oxidised cellulose and the excess CAN most likely attack CDI molecules to generate CDI free radicals (•CD). Thus, additional reactions leading to further graft copolymerisation and network formation via crosslinking according to Eq. (1(b)) and (1(c)) may also take place. However, the linkage between cellulose and CDI might also occur through esterification as a result of higher temperatures (Eq. (2(a))), and thermal graft copolymerisation and crosslinking, as shown by Eq. (2(b)) and (2(c)), may occur due to the high curing temperature.

3.2.4. Performance evaluation of modified fabrics

3.2.4.1. Effect of CAN concentration. To investigate the effect of CAN concentration on the mechanical strength and wrinkle ability of modified samples, the fabrics were treated with different concentrations of CAN, padded with 20 g/L CDI and then dried and cured at 165 °C for 1 min. The tensile strength loss and the relative wrinkle recovery angle as a function of applied CAN concentration are presented in Fig. 3a. According to the results obtained for the

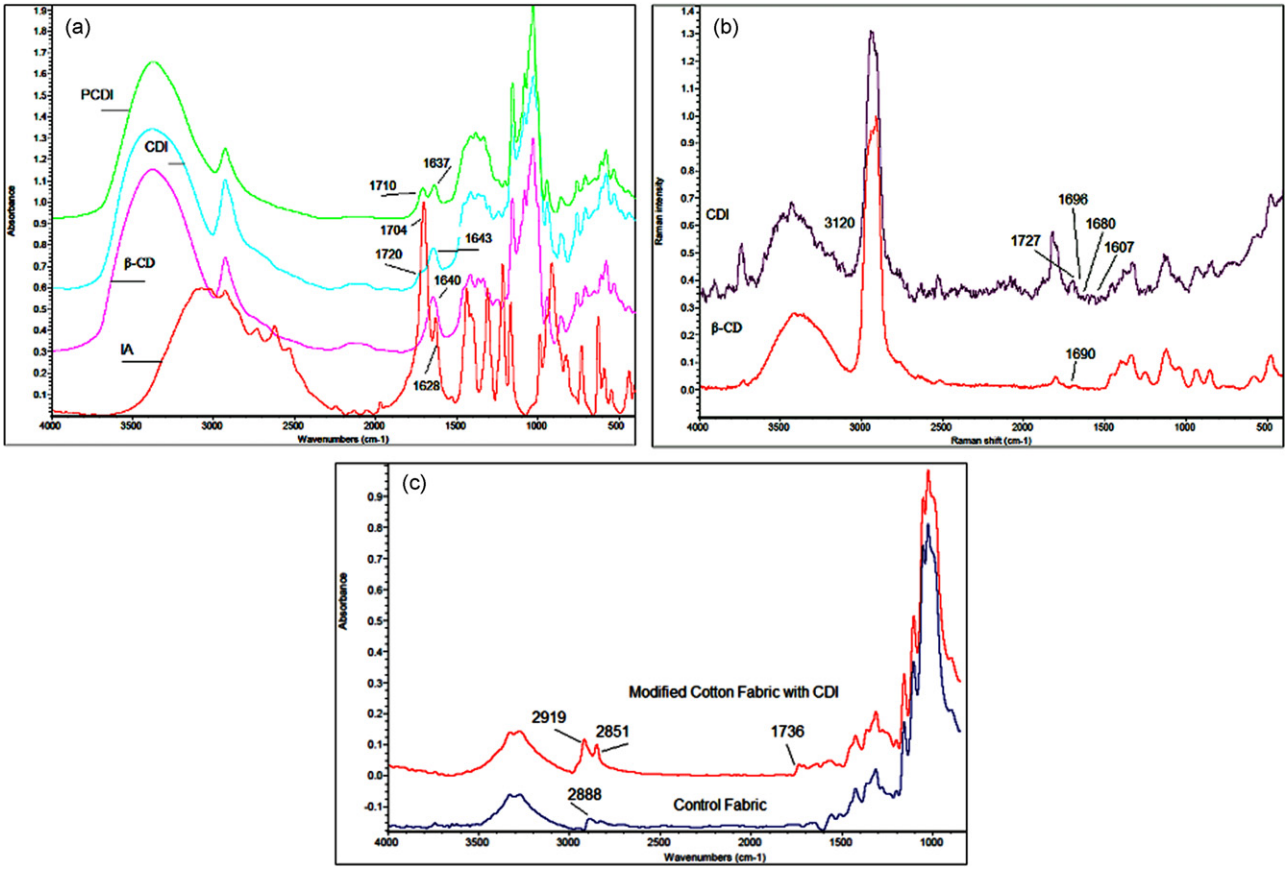


Fig. 2. (a) FTIR spectra of IA, β-CD, CDI and PCDI, (b) Raman spectra of β-CD and CDI and (c) ATR-FTIR spectra of control and grafted fabric with CDI.

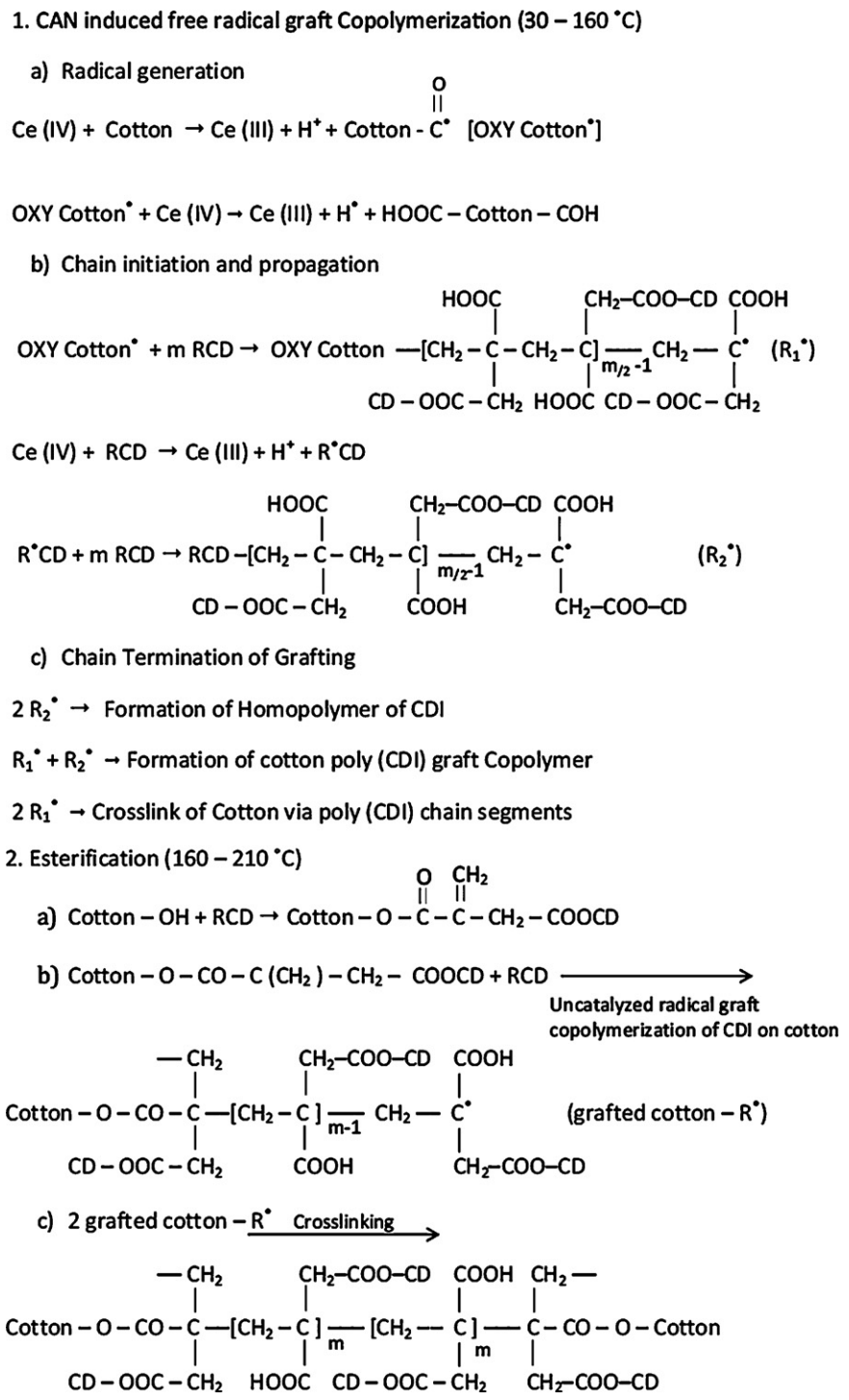
tensile strength loss of a sample treated with this procedure without the application of CAN and CDI, there was not a significant difference between this sample and the control fabric; however, the sample treated with CDI without CAN showed a large decrease in its tensile strength. It seems that as the fabric was impregnated with an acidic solution of CDI (pH ~ 4) and then exposed to heat, its mechanical strength strongly decreased due to the synergetic degradation effect of acidic media and heating. In addition, despite the fact that the cotton fabric lost about 34% of its original tensile strength when it was treated with (0.016 mol/L) CAN alone, the results indicate that the tensile strength loss of the modified fabric with CDI decreased significantly from 32% to 12% as the CAN concentration was increased from zero to 0.016 mol/L. It is clear that the significant loss in fabric tensile strength caused by CAN is due to the oxidative effects of CAN on cotton. Thus, although it is expected that the tensile strength loss would increase with increasing CAN concentration, due to the graft copolymerisation of CDI, according to mechanism (1) in Scheme 3, the tensile strength increases and compensates for the oxidation effect of CAN. Furthermore, when the CAN concentration was increased beyond its threshold and up to 0.03 mol/L, the fabric lost more of its tensile strength. This behaviour may be because higher concentrations of CAN are able to penetrate through more of the amorphous region of cellulose, even though the monomers aggregate on the surface. Hence, it could be assumed that, in this situation, the cellulosic chains prefer to crosslink with each other instead of grafting with CDI and that their probability of recombination increases. Thus, the tensile strength decreased rapidly. Therefore, in the moderate range of CAN concentration, although the tensile strength loss of the modified cotton fabric is attributed to cellulose degradation, the graft copolymerisation of CDI could be responsible for the compensating increase in tensile strength.

The effect of CAN concentration on the wrinkling ability of the modified samples is also shown in Fig. 3a. It was found that if the wrinkle recovery angle (WRA) of the treated sample was lower than that of the control fabric, the relative WRA would be positive such

Table 2
Characteristics of control and modified cotton fabrics.

Sample	Method of CDI grafting	Concentration of CDI (g/L)	Tensile strength (N)	Elongation at break (%)	WRA[a] (°)	Decrease in phenolphthalein absorbance intensity (%)
Control cotton fabric	–	–	384 (10.6)	9.73 (0.13)	192.36 (4.57)	–
Treated fabric with CAN alone	–	–	254 (14.8)	7.54 (0.37)	198.34 (3.06)	4.21
Grafted fabric with CDI	Pad thermofixation	20	365 (6.4)	9.39 (0.05)	177.34 (3.61)	12.41
Grafted fabric with CDI	Semi-continuous pad-batch	20	373 (17.9)	10.27 (0.19)	165.68 (2.28)	16.63
Grafted fabric with CDI	Batch	100	367 (18.7)	9.70 (0.31)	188.54 (3.56)	16.41

The values in parenthesis are showed standard deviation.
[a] These values are related to the wrinkle recovery angle of warp + weft totally.



Scheme 3. Reaction scheme showing modification of cotton cellulose under the influence CAN and heating for graft copolymerisation and crosslinking (CDI is indicated as RCD).

that the wrinkling ability would increase. It can be observed that the wrinkling ability of the fabric treated without CAN rose slightly due to the acidic degradation of CDI at high temperature. Additionally, the relative WRA shows a decreasing trend as the CAN concentration increases. At low CAN concentrations, due to the oxidation effect of CAN, the hydrophilicity of the cellulose increased, but by further increasing the concentration, the initiator can penetrate through more of the amorphous region and the probability of radical recombination and cellulosic chain crosslinking increases. Therefore, it seems that a lower concentration of CAN is useful due to its lower effect on the wrinkling ability of fabrics.

3.2.4.2. Effect of curing temperature. Fig. 3b depicts the effect of the curing temperature on the tensile strength loss and the relative WRA of fabric treated with CDI. To investigate the effect of the curing temperature on the mechanical strength and wrinkle ability of the modified samples, the fabrics were treated with (0.016 mol/L) CAN, padded with (20 g/L) CDI and then dried and cured for 1 min at different temperatures. The results obtained indicate that the decrease in tensile strength loss became moderate as the curing temperature was increased from 120 to 165 °C; however, the rate of tensile strength loss increased substantially for higher curing temperatures of up to 210 °C. These results suggest that at lower

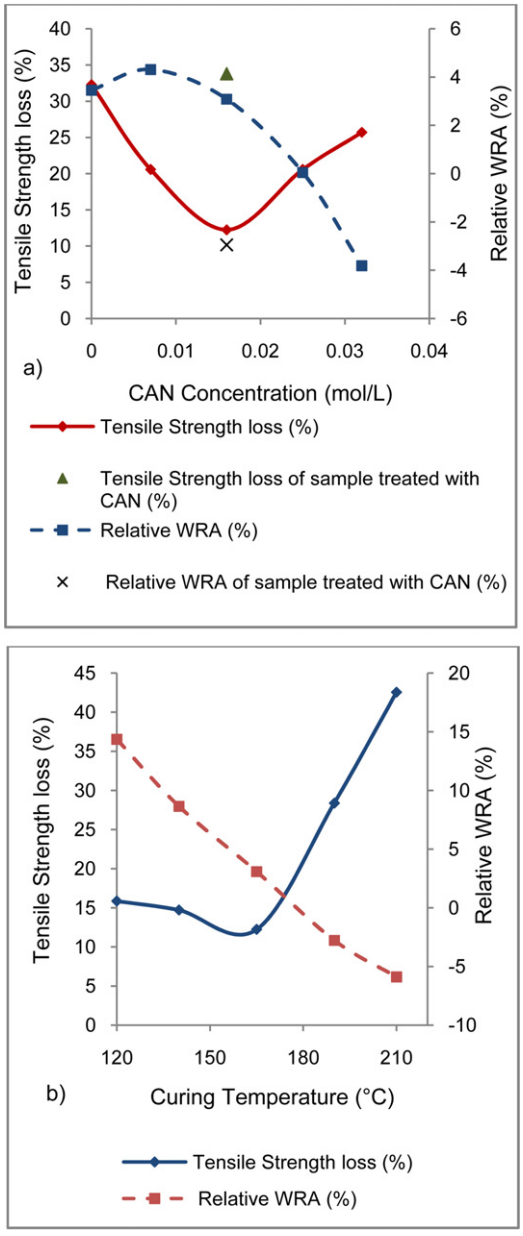


Fig. 3. Tensile strength loss and relative WRA of the cotton fabric pretreated with (a) CAN in different concentrations then treated with or without CDI, dried and cured at 165 °C for 1 min and (b) 0.016 mol/L CAN then treated with CDI, dried and cured at the different temperatures for 1 min.

temperatures, graft copolymerisation of CDI on the surface in accordance with mechanism (1) in Scheme 3 is more likely than the other mechanisms. However, at high temperatures, the distribution of CDI as a crosslinking reagent across the fabric surface according to mechanism (2) in Scheme 3 negatively affected the mechanical strength.

The effect of curing temperature on the wrinkle ability of the fabrics modified with CDI is also illustrated in Fig. 3b. It can be observed that there was a marked decrease in the relative WRA and in the wrinkle ability of the modified fabrics with increasing curing temperature. Therefore, it seems that at lower temperatures, the grafting copolymerisation of CDI on cellulose is probable, although a greater decrease in tensile strength and an increase in wrinkle recovery angle can be achieved by further increasing the curing temperature, due to the crosslinking action of the cellulosic chains. These behaviours imply that the optimum conditions for the lowest tensile strength loss and the lowest effect on the wrinkle ability correspond to lower curing temperatures.

3.2.4.3. Optimum conditions. In this study, the effect of other factors, such as the curing time, temperature and time of drying, were also investigated. Based on our results, it can be assumed that, although factors such as CAN concentration and curing temperature are more significant for the graft copolymerisation of CDI, other factors may control the mechanism for the modified fabric with improved performance. In addition, the application of different CDI concentrations in this procedure showed that, as CDI is not able to dissolve uniformly at concentrations higher than 30 g/L, higher CDI concentrations have a statistically insignificant effect on the performance of the modified fabrics. Therefore, for this purpose, the optimum conditions were estimated to occur for 0.016 mol/L CAN, 20 g/L CDI, drying at 80 °C for 2.5 min and curing at 165 °C for 1 min. The characterisation results of a sample prepared under these conditions are shown in Table 2.

3.2.5. Field emission scanning electron microscopy (FE-SEM)

FE-SEM was conducted to investigate the grafting contents of the cotton fibres. According to the SEM micrographs, it was clear that the surface morphology of the grafted cellulosic fibres with CDI differed from the control fibres. The nanoparticles (diameter: ~470 nm) on the modified fibres surface in the resulting micrographs confirmed homogenous and uniform grafting of CDI.

3.2.6. Evaluation of inclusion complex formation on the surface

Images of a drop of water on the surface of the control and modified cotton fabrics after treatment with cyclohexane were obtained using an optical contact angle measuring instrument. It is obvious that the fabric modified with CDI became highly hydrophobic after treatment with cyclohexane, as its contact angle (approximately 124°) increased in comparison with the control fabric (approximately 88°). Therefore, it can be assumed that, although the modified fabric is completely hydrophilic, it has the capability of forming inclusion complexes with hydrophobic molecules.

4. Conclusion

A reactive β-cyclodextrin derivative was synthesised by reacting β-cyclodextrin and itaconic acid. Its structure was characterised using solubility studies, elemental and thermal analysis and NMR, FT-IR and Raman spectroscopy methods, which showed agreement with the expected results. In accordance with the results obtained from instrumental analysis, itaconic acid can be reacted with cyclodextrin via an esterification reaction, and the presence of a vinyl group in this compound was found to be useful for producing a new reactive cyclodextrin that can chemically bond onto the surface of cellulose fibres via graft copolymerisation. By controlling the mechanism for grafting the reactive cyclodextrin on the cellulose, this modification does not show any negative effect on the performance of cotton fabric. The results of inclusion complex formation and SEM also demonstrated the accessibility of the cyclodextrin cavities for molecular encapsulation on the surface of cotton fabric.

Acknowledgements

The work was financially supported by Amirkabir University of Technology (AUT). The authors are grateful to the Collage of Textile (COT) and North Carolina State University for providing some research facilities. Brigit Andersen, the manager of the Analytical Laboratory at COT is thanked for her useful advice and suggestions.

References

Bilal, M., de Brauer, C., Claudy, P., Germain, P., & Létoffé, J. (1995). β-Cyclodextrin hydration: A calorimetric and gravimetric study. *Thermochimica Acta*, *249*, 63–73.

Buschmann, H. J., Deuter, U., Knittel, D., & Schollmeyer, E. (1988). The use of cyclodextrins in textile process. *Journal of Industrial Textiles*, *89*, 554–561.

Buschmann, H. J., Knittel, D., & Schollmeyer, E. (2001). New textile applications of cyclodextrins. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, *40*(3), 169–172.

Cireli, A., & Yurdakul, B. (2006). Application of cyclodextrin to the textile dyeing and washing processes. *Journal of Applied Polymer Science*, *100*, 208–218.

Croft, A. P., & Bartsch, R. A. (1983). Synthesis of chemically modified cyclodextrins. *Tetrahedron*, *39*(9), 1417–1474.

Del Valle, E. M. (2004). Cyclodextrins and their uses: A review. *Process Biochemistry*, *39*, 1033–1046.

Denter, U., & Schollmeyer, E. (1996). Surface modification of synthetic and natural fibres by fixation of cyclodextrin derivatives. *Journal of Inclusion Phenomena and Molecular Recognition in Chemistry*, *25*(1-3), 197–202.

Dodziuk, H. (2006). *Cyclodextrins and their complexes: Chemistry, analytical methods, applications*. Weinheim: Wiley-VCH Verlag GmbH.

El-Alfy, E., Khalil, M., & Hebeish, A. (1981). Ce(IV)-induced polymerization of allyl methacrylate with cotton cellulose. *Journal of Polymer Science: Polymer Chemistry Edition*, *19*(12), 3137–3143.

Freudenberg, K., & Cramer, F. (1948). Die konstitution der schardinger-dextrine α, β und γ. *Zeitschrift fur Naturforschung B*, *3*, 464–468.

Gaffar, M. A., El-Rafie, S. M., & El-Tahlawy, K. F. (2004). Preparation and utilization of ionic exchange resin via graft copolymerization of β-CD itaconate with chitosan. *Carbohydrate Polymers*, *56*(4), 387–396.

Goel, A., & Nene, S. (1995). Modifications in the phenolphthalein method for spectrophotometric estimation of beta-cyclodextrin. *Starch/Stärke*, *47*, 399–400.

Grechin, A. G., Buschmann, H.-J., & Schollmeyer, E. (2007). Quantification of cyclodextrins fixed onto cellulose fibers. *Textile Research Journal*, *77*(3), 161–164.

Hajny, G., & Reese, E. (1969). *Cellulases and their applications*. Washington, DC: American Chemical Society.

Jozwiakowski, M. J., & Connors, K. A. (1985). Aqueous solubility behavior of three cyclodextrins. *Carbohydrate Research*, *143*, 51–59.

Klemm, D., Philipp, B., Heinze, T., Heinze, U., & Wagenknecht, W. (1998). *Comprehensive cellulose chemistry. Fundamentals and analytical methods* Weinheim: Wiley-VCH Verlag GmbH.

Kumbasar, E. P., Atav, R., & Yurdakul, A. (2007). Equalizing effect of β-cyclodextrin on dyeing of polyamide 6,6 woven fabrics with acid dyes. *Journal of Applied Polymer Science*, *103*, 2660–2668.

Lee, M., Yoon, K., & Ko, S.-W. (2000). Grafting onto cotton fiber with acrylamidomethylated β-cyclodextrin and its application. *Journal of Applied Polymer Science*, *78*, 1986–1991.

Loftsson, T., & Masson, M. (2001). Cyclodextrins in topical drug formulations: Theory and practice. *International Journal of Pharmaceutics*, *225*, 15–30.

Misiuk, W., & Zalewska, M. (2008). Study on the inclusion interactions of β-cyclodextrin and its derivative with clomipramine by spectroscopy and its analytic application. *Analytical Letters*, *41*, 543–560.

Nazi, M., Malek, R., & Moghaddam, M. (2010, Spring). Interactive Effects of synthesis parameters on reaction of β-cyclodextrin nanocapsule with itaconic acid. In *The Fiber Society International Conference* Bursa, Turkey.

Okabe, M., Lies, D., Kanamasa, S., & Park, E. Y. (2009). Biotechnological production of itaconic acid and its biosynthesis in Aspergillus terreus. *Applied Microbiology and Biotechnology*, *84*, 597–606.

Otta, K., Zsadon, B., Farago, J., Szejtli, J., & Tudos, F. (1988). *Proceedings of the IVth International Symposium on Cyclodextrins* (pp. 139–143).

Ouziel, P., & Kulke, T. (2007). Patent No. 20070277328. United States Patent.

Pöpping, B., & Deratani, A. (1992). Synthesis of cyclodextrins with pendant chlorinated groups. Reaction of β-cyclodextrin with epichlorohydrin in acidic medium. *Die Makromolekulare Chemie, Rapid Communications*, *13*, 237–241.

Pottenger, C., & Johnson, D. (1970). Mechanism of cerium (IV) oxidation of glucose and cellulose. *Journal of Polymer Science Part A-1: Polymer Chemistry*, *8*(2), 301–318.

Raffaini, G., & Ganazzoli, F. (2007). Hydration and flexibility of α-, β- and γ-cyclodextrin: A molecular dynamics study. *Chemical Physics*, *333*, 128–134.

Reuscher, H., & Hinsenkorn, R. (1996). BETA W7 MCT-new ways in surface modification. *Journal of Inclusion Phenomena and Molecular Recognition in Chemistry*, *25*(1-3), 191–196.

Reuscher, H., Hirsenkorn, R., & Haas, W. (1998). Patent No. 5728823. United States Patent.

Sanger, W. (1980). Cyclodextrin inclusion compounds in research industry. *Angewandte Chemie International Edition in English*, *19*(5), 344–410.

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.

Schmidt, A., Buschmann, H. J., Knittel, D., & Schollmeyer, E. (2005). Patent No. 20100267300. United States Patent.

Schneider, H. J., Hacket, F., & Rüdiger, V. (1998). NMR studies of cyclodextrins and cyclodextrin complexes. *Chemical Review*, *98*, 1755–1785.

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.

Shibusawa, T., Okamoto, J., Abe, K., & Sakata, K. (1998). Inclusion of azo disperse dyes by cyclodextrins at dyeing temperature. *Dyes and Pigments*, *36*(1), 79–91.

Song, L., Teng, C., Xu, P., Wang, H., Zhang, Z., & Liu, Q. (2008). Thermal decomposition behaviors of β-cyclodextrin, its inclusion complexes of alkyl amines, and complexed β-cyclodextrin at different heating rates. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, *60*, 223–233.

Szejtli, J. (1982). *Cyclodextrins and their inclusion complexes*. Budapest: Akademiai Kiado Publisher.

Szejtli, J. (1988). *Cyclodextrin technology*. Dordrecht: Kluwer Academic Publishers.

Szejtli, J. (1996). *Comprehensive supramolecular chemistry* Pergamon: J.L. Atwood.

Szejtli, J. (1997). Utilization of cyclodextrins in industrial products and processes. *Journal of Materials Chemistry*, *7*(4), 575–587.

Szejtli, J. (1998). Introduction and general overview of cyclodextrin chemistry. *Chemical Reviews*, *98*, 1743–1753.

Szejtli, J. (2003). Cyclodextrins in the textile industry. *Starch/Stärke*, *55*, 191–196.

Tabushi, I. (1982). Cyclodextrin catalysis as a model for enzyme action. *Accounts of Chemical Research*, *15*, 66–72.

Vögtle, F. (1991). *Supramolecular chemistry, an introduction*. New York: John Wiley & Sons.

Voncina, B., Vivod, V., & Jausovec, D. (2007). β-Cyclodextrin as retarding reagent in polyacrylonitrile dyeing. *Dyes and Pigments*, *74*, 642–646.

Wang, C. X., & Chen, S. L. (2005). Fragrance-release property of β-cyclodextrin inclusion compounds and their application in aromatherapy. *Journal Industrial Textiles*, *34*, 157–166.

Yang, C. Q., & Wang, X. (1996). Formation of cyclic anhydride intermediates and esterification of cotton cellulose by multifunctional carboxylic acids: An infrared spectroscopy study. *Textile Research Journal*, *66*(9), 595–603.

Yoshinaga, M. (1992). Patent No. EP19910909359. European Patent.