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Grafting Modification of Natural Fibres with Cyclodextrin

DOI: 10.5604/01.3001.0014.3793

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Abstract
Over the years, a multiplicity of grafting modification techniques have been studied to combine the adsorption and wettability of natural fibres with the capacity of cyclodextrins (CDs) to form inclusion complexes. The fixation of CDs on fibres is possible using crosslinking agents or reactive derivatives of cyclodextrins. Various crosslinking chemicals are suitable to bind the hydroxyl groups of non-reactive cyclodextrins with those of natural fibres by way of spraying, padding, surface coating, and impregnation. Nano-composite dense polymer film could also be formed to anchor the cyclodextrin on the natural fibre surface by the methods of hydrogen binding or covalent binding in sol-gel. A vinyl monomer such as glycidyl methacrylate was used to form polymer coatings due to the pendant epoxy group coupled with the –OH of cyclodextrin and natural fibres. This review also focused on the derivatives of CDs with the reactive group reacting with the hydroxyl groups of natural fibres.

Key words: *grafting modification, cyclodextrin, natural fibre, crosslinking chemical, polymeric binder, reactive cyclodextrin.*

Introduction

Due to the conformation of the hydrophobic inner part and the hydrophilic outer part of the cyclodextrins ring molecules, consisting of 6, 7 or 8 glucopyranose units, referred to as α-, β- or γ-CDs respectively, host-guest complexes of cyclodextrins with molecules of suitable structure were build. There is rising interest in applying cyclodextrins and complexes in the manufacturing of functional materials with various properties, such as anti-microbial [1], adsorption of unpleasant odours [2] and metal salts [3], fragrance complexation and release [4], drug sustained release [5], enhancing the behaviour of textile fabrics [6], etc.

Natural fibres like cellulose and protein fibre possess fascinating molecules with synergistic properties due to active groups such as hydroxyl, amino, carboxyl and thiol groups. Natural fibres have been widely applied as suitable matrix in preparing the above-mentioned functional materials containing CDs, which combine the adsorption and wettability of natural fibres with the capacity of CDs to form inclusion complexes. In general, to form these type of structures and satisfy the desired fastness against washing, natural fibres have been modified by different types of CDs, with a permanent finishing effect. Accordingly, modification can be accomplished by chemical or physical means. Since natural fabrics are in direct contact with human skin, the toxic specification of cyclodextrin was studied [7]. Results indicate that they may be harmful to the human body in very high concentrations. Since November 13, 2000, β-CD has been introduced as a food additive in Germany. According to OECD experiments, this compound shows no allergic impact [8-10].

Nowadays, researchers have paid attention to finding new ways of functionalising natural fibres with supramolecular, such as cyclodextrins to improve their properties as well as the slow release of fragrances, and antibacterial, antibiotics, and insecticide delivery. A variety of chemical and physical processes exist for the modification of textile fibres with cyclodextrins, by way of spraying, padding, surface coating, and impregnation to bind cyclodextrins onto natural fibres. The structure of original CDs showed that it cannot form a direct covalent bond with fibres. The fixation of CDs on fibres is possible using reactive derivatives of cyclodextrins or crosslinking agents.

This review focuses on advances in the modification of natural fibres with CDs. Relevant aspects regarding methods of modification suitable for non-reactive CDs and reactive CDs are presented (shown in ***Figure 1***).

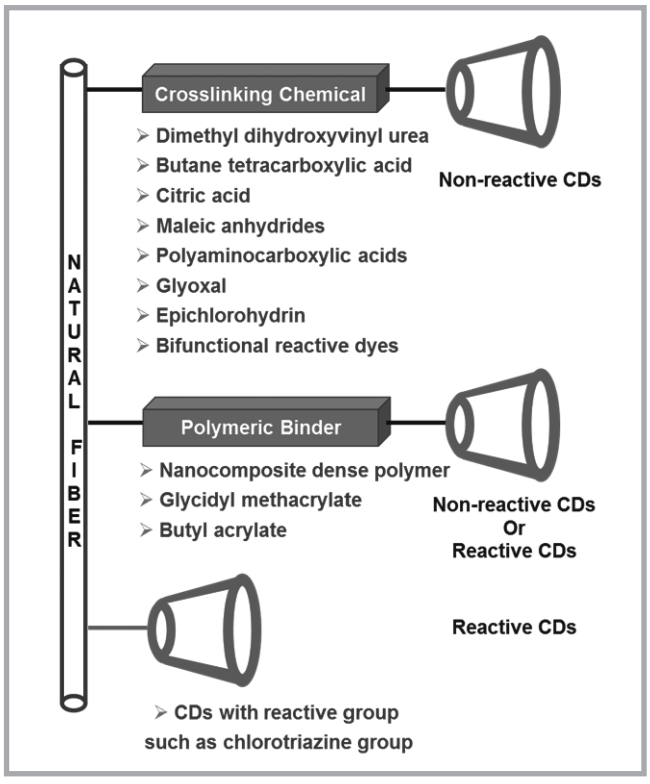

Figure 1. *Graft modification of natural fibres with non-reactive CDs or CDs with reactive groups.*

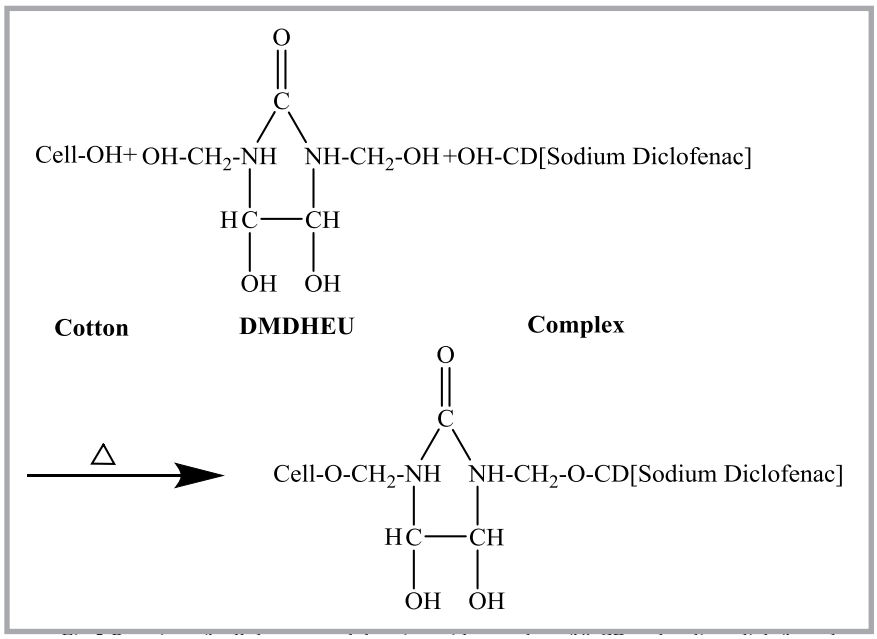

Figure 2. *Reaction of cellulose wound dressing with a complex of β-CD and sodium diclofenac by means of a cross-linking agent based on DMDHEU [12].*

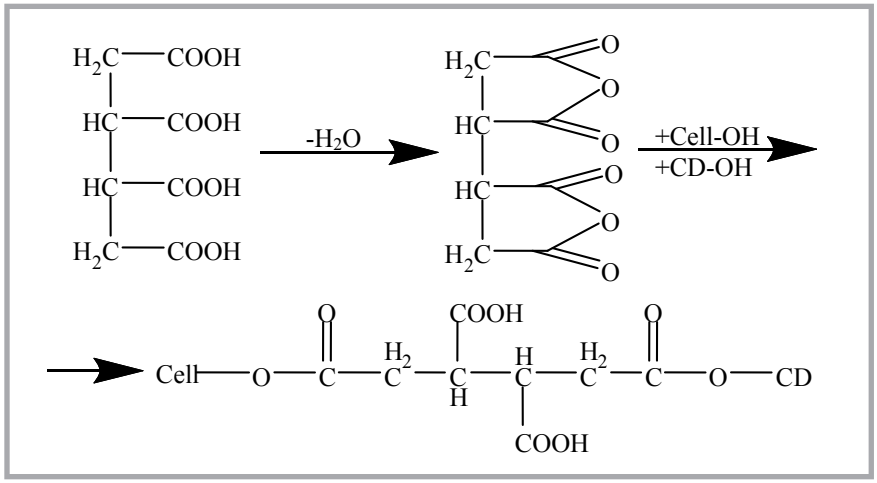

Figure 3. *Proposed grafting reaction of β-CD onto hydroxyl groups of cellulose via BTCA [14].*

Modification with non-reactive CDs by chemical crosslinking

Chemical cross-linking methods that involve the use of native CDs or reactive derivatives and cross-linkers suitable to bind the hydroxyl groups of CDs with those of natural fibres have been developed, rendering high yields of grafting. Crosslinking chemicals are compounds with bi- or multifunctional groups capable of reacting with two other compounds and forming covalent bonds. These chemicals can also attach chemical compounds to fibres. The most conventional crosslinking agents for non-reactive CDs are N-methylol compounds and polycarboxylic acids combined with salts of weak acids as catalyst.

Dimethyl dihydroxyvinyl urea (DMDHEU)

The most widely used crosslinking agents have been N-methylol agents or formaldehyde reactants, DMDHEU in particular, due to their efficiency and low price [11].

A cross-linking agent based on DMDHEU was used for modifying wound dressings with β-cyclodextrin [12]. The reaction of methylol groups of DMDHEU with hydroxyl groups of cellulose and β-CD (***Figure 2***) was achieved by padding cellulose textiles using different solutions with a wet pick up of 70% and cured at 150 °C for 5min. The absence of DMDHEU leads to the forming of a film of complex on the wound dressing without binding to the cellulose wound dressing. Therefore, the complexes which are not linked to the wound dressing could release themselves easily in release conditions. The drug releases itself rapidly from samples without a crosslinking agent even in the first 8 hr of testing. There are no linkages between the complex and the wound dressing without a cross-linking agent, and the complex only attached itself physically to the wound dressing. Therefore, the unbounded complex leaves the wound dressing quickly when placed in inflammation conditions (aqueous solution with pH = 7.4). The presence of β-CD in the complex along with the drug extends the release time, prolonging it to 48 hr.

Butane tetra carboxylic acid

As the effects of formaldehyde include carcinogens in DMDHEU modification, efforts have been made to develop formaldehyde-free alternatives, including mainly ionic crosslinking, polycarboxylic acid and glyoxal.

Poly (carboxylic acids) have been applied as formaldehyde-free crosslinking agents to improve the performance of natural fibres. Among the poly (carboxylic acids), 1,2,3,4-butane tetra carboxylic acid (BTCA) with four carboxylic acid groups is a non-toxic carboxylic acid that is able to react with the hydroxyl groups of cellulose fibres and form stable ester bonds [13]. Esterification can occur with heat alone or can be accelerated by the presence of catalysts such as sodium hypophosphite (SHP).

Voncina [14] also chose the pad-dry-cure process to modify cellulose fabrics with β-CD. The cellulose fabrics were padded by different baths containing β-CD, BTCA and SHP with a pick-up of 150%, dried at 110 °C for 10 min, and cured at 170 °C for 3 min. The cellulose fabrics were successfully grafting modified with β-CD based on the reaction of carboxyl groups of BTCA with hydroxyl groups of cellulose and β-cyclodextrin, as shown in ***Figure 3***.

Apart from individual cellulose fibres grafted by CDs, as mentioned above, complex CD-cellulose networks were formed with cellulose fibres connected by CDs and cellulose fibres linked together via BTCA, resulting in less solubility in the "super phosphoric" acid solution. It is shown that an increase in the concen-

trations of both the initial concentration of CD and BTCA, the grafting ratio of β-CD to the cellulose backbone also increased. The influence of the BTCA mass can be neglected due to the low molecular mass of BTCA compared to the molecular mass of β-CD [15].

The reaction of β-CD and cellulose with BTCA can involve either two carboxyl groups or all four. While the cure temperature near the melting point of BTCA generally leads to greater fastness to washing because the formation of ester bonds between cellulose and BTCA was more effective at 180 °C [16].

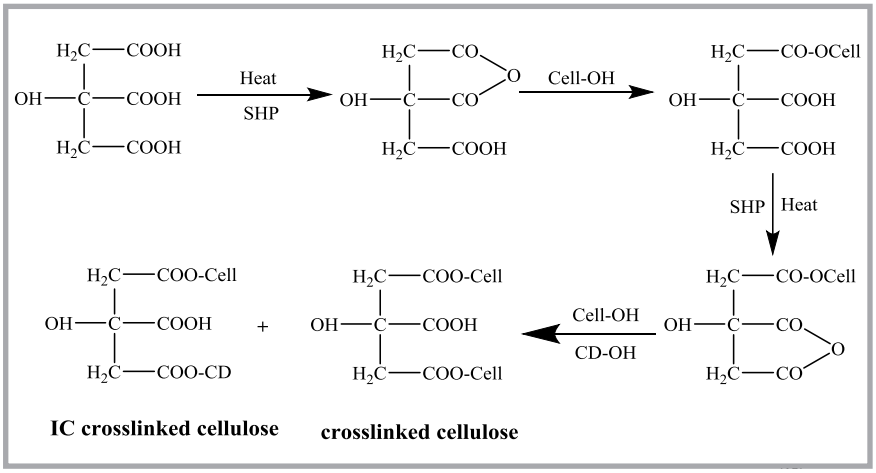

Figure 4. *Cross-linking mechanism of cellulose and β-cyclodextrin inclusion complex [17].*

Citric acid

Citric acid (CA) is also a non-toxic carboxylic acid with three carboxylic acid groups and with characteristics of being inexpensive, commercially available on the market and eco-friendly. By the pad-dry-cure process, CA can form a 5-membered cyclic anhydride intermediate in the presence of SHP and then forms an ester bond with the alcoholic group of cyclodextrin and natural fibres (***Figure 4***). Increasing the CA and/or SHP concentrations will increase the carboxyl content of the treated fibres. Such an increase reflects the higher efficiency of CA at higher concentrations of SHP. Increasing the amount of citric acid in the modifying bath could increase the availability and accessibility of CA molecules in the moiety of the fabric that can react with the cellulose hydroxyls. Raising the curing temperature facilitates the formation of citric anhydride intermediate. The latter reacts more easily with the cellulosic hydroxyl to form ester linkage; however, a higher curing time and temperature leads to the yellowing of the fabric [17,18].

Due to the use of polycarboxylic acids, the solubility of CD (18 $g \cdot L^{-1}$ at 20 °C) was increased above to 100 $g \cdot L^{-1}$, exceeding the new limit of solubility and forming an oversaturated system. This observation can also be explained by the saturation of the available cellulose hydroxyl groups in position 6 [19]. Gawish [20] studied the effects of process parameters on the add-on ratio of β-CD on wool fabric in the presence of CA and SHP or sodium di-hydrogen phosphate (SDP) using the pad-dry-cure technique. Nonyl phenol ethoxylate nonionic wetting agent and silicone softener were used for better absorption and attachment of β-CD on wool fibres. As the curing temperature and time increase, the percentage add-on of β-CD onto wool fabrics and the yellowness index of the fabrics also increase. SHP and SDP act as retarders and not as catalysts, as they could decrease the cross-linking between wool and citric acid. This result could be attributed to the capability of these two compounds to accelerate both the formation of the cyclic anhydride intermediate and the reaction between the anhydride intermediate and β-CD instead of the reaction between cyclic anhydride and wool because β-CD has a large number of free hydroxyl groups, which leads to a decrease in the available amount of citric acid, that is, the cross-linking agent between the wool and β-CD.

Low temperature oxygen plasma was used to improve the absorption of β-CD on wool fibres. Woollen fabric samples were pretreated using radio frequency low pressure plasma equipment with oxygen gas, and then modified with solutions containing β-CD, CA and SHP by the pad-dry-cure process. Response surface methodology was used to optimise the process of grafting β-cyclodextrin on wool fabric. Besides the concentration of β-CD and CA, two other independent factors – plasma time and power, had an increasing effect on the modification evaluated by weight gain [21].

By the pad-dry-cure technique, Mehraz [22] modified silk fabric with β-cyclodextrin using CA as the cross-linking agent. The modifying reaction also occurs through the dehydration of CA under the curing temperature, which yields a cyclic anhydride intermediate which can react with the hydroxyl groups of silk fibroin and β-CD by esterification reaction. The hydroxyl group of Glycine is the major functional group that is responsible for the esterification of silk fibroin. Both CD–CA–CD and Silk–CA–Silk crosslinking may take place during the modifying process, but CD–CA–CD complexes are removed during the washing process, and the crosslinking of silk-CA-silk is negligible compared to that of CD–CA–Silk due to the higher number of hydroxyl groups of β-CD than those of silk fibroin.

Maleic anhydrides

Maleic anhydride is an unsaturated polycarboxylic acid which can react with primary hydroxyl groups of cotton cellulose and β-CD to produce heterogeneous esterification products under the influence of an acid liberating catalyst like tri-sodium phosphate. Unsaturated maleic anhydride can also undergo free-radical polymerisation reaction when initiated by a relevant catalyst like ammonium peroxodisulphate. Due to this dual reaction, it is possible that a complex cross-linked network is formed. β-CD can also be incorporated in cotton fabric following the pad-dry-cure technique, employing maleic anhydride (an unsaturated dicarboxylic acid) as the modifying agent under the dual influence of the free radical polymerization catalyst ammonium peroxodisulfate [$(NH_4)_2S_2O_8$] and esterification catalyst tetrasodium pyrophosphate ($Na_4P_2O_7$). β-CD can be esterified if treated with maleic anhydride due to the presence of hydroxyl groups in β-cyclodextrins [23].

Polyaminocarboxylic acids

Polyaminocarboxylic acids (PACAs) are novel formaldehyde-free crosslink-

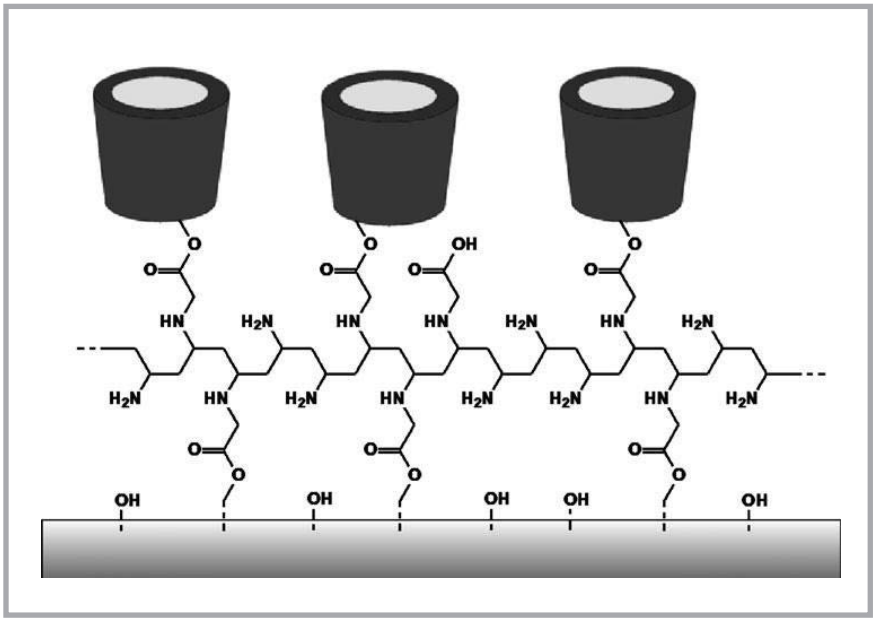

Figure 5. *Schematic presentation of cyclodextrin fixation onto cotton fabric using PACAs [24].*

ing agents for the fixation of β-CD onto cotton fabric, and are easily synthesised by the carboxylation of polyamines. PACAs can be fixed onto cotton fabrics via esterification of the hydroxyl groups of cellulose chains. Stepwise fixation and simultaneous fixation were applied for the fixation of β-CD onto cotton using PACAs. In stepwise fixation, the cotton fabrics were firstly treated with PACAs and then dipped and padded with a solution of β-CD and sodium hypophosphite. While PACAs and β-CD were employed on cotton fabrics simultaneously in the latter method [24]. In both cases two reactions occur: that between PACA and the hydroxyl groups of the cotton fabric (eaterification of cotton) and that between PACA and the hydroxyl groups of the CD molecules (fixation of CD onto cotton textile via esterification, see ***Figure 5***).

Glyoxal

Glyoxal is another formaldyhyde free crosslinking agent with the advantages of low cost, ready availability, high functionality, and high solubility in water. The dialdehyde groups in the glyoxal molecule can produce crosslinks through hemiacetal or acetal formation. An ether bond is formed between glyoxal and a hydroxyl group on the β-CD molecule. When the molecule of cotton cellulose reacts with the β-CD/glyoxal mixture, an ether bond is formed between the glyoxal and the hydroxyl group of the cotton cellulose in the fabric. β-CD is thus bonded by ether linkages to cellulose molecules in the cotton fabric [25].

For glyoxal modification, drawbacks include strength loss and yellowing of the treated fabrics. Crosslinking between cellulose molecules causes fibre embitterment, thus reducing the mechanical properties of the treated fabric. The conventional curing system may also contribute to a decrease in crosslinked fabric's mechanical strength because of the uneven heating, which leads to non-uniform crosslink distribution throughout the fabric.

Hebeish [25] applied microwave curing as a possible alternative to conventional curing to improve the mechanical properties of crosslinked cotton textiles. This method can uniformly generate heat throughout a textile substrate impregnated and padded with solutions containing glyoxal, β-CD, $Al_2(SO4)_3$ and tartaric acid. Under the influence of the catalyst and uniform curing, the cotton cellulose, glyoxal and β-CD in the fabric react as described above to form covalently bonded networks, which decreases strength losses without affecting the colour intensity.

Epichlorohydrin

Epichlorohydrin is largely used for covalent bonding between epoxygroups of epichlorohydrin and hydroxyl groups of CDs and cellulose. Cellulose fabric is firstly swelled in an NaOH bath and then modified with epichlorohydrin in a bath containing NaOH and β-CD [26, 27].

Szejtli firstly reported the grafting of CDs onto cellulose fibres using epichlorohydrin as a cross-linking agent [28]. Neto [29] succeeded in modifying cellulose fabric by adding epichlorohydrin solution together with the fabric without alkalescent pretreatment. As compared with other crosslinking agents, the reaction between the crosslinking agent, cellulose and β-CD can proceed at a lower temperature of 40 °C by the impregnation method, which can avoid fibre damage at high temperatures.

Bifunctional reactive dyes

The modification of cellulose fabric with β-CD was also reported by means of heterobifunctional reactive dyes containing monochlorotriazine and vinyl sulfone reactive groups.

Wang [30] anchored β-cyclodextrin molecules to cellulose using heterobifunctional reactive dyes to provide a chemical linkage. Dyeing and modifying of the cotton fabrics were simultaneously carried out in dyebaths containing heterobifunctional reactive dyes and β-CD. The chemical structure of the dye determines its reactivity to both cellulose and β-CD. The hydroxy groups on the cellulose and β-CD show similar reactive behaviour. A β-cyclodextrin molecule can only become anchored to the fibre if one of the reactive groups on the dye is able to react with one of its hydroxy groups and the other with a hydroxy group on cellulose. In this way, the dye molecule acts as a crosslinker. An alternative possibility is that a β-cyclodextrin molecule might be anchored by two dye molecules, forming a longer bridge. Any of these dyes is capable of reacting with the hydroxy groups on both cellulose and β-cyclodextrin under alkaline dyeing conditions. At the same time, the active chlorine atoms on the triazine ring can also react with each of the two hydroxy groups (one on β-cyclodextrin and the other on cellulose). Blue dye was found to anchor more β-CD to the fabric than the other dyes under similar conditions. Although all of the dyes are bifunctional, each showed different reactivity to cellulose and β-CD due to the different structure of their chromophores and bridge groups. It is clear that the β-CD concentration on the fabric increases with an increase in the initial concentration of β-CD in the dyebath. However, when the concentration of β-CD on fibre reaches a certain value, the effect of the concentration becomes less apparent.

Agrawal [31] used heterobifunctional and homobifunctional reactive dyes to modify cotton with β-CD. It is clear from the research results that crosslinking with homo-bi-functional reactive dyes shows better attachment than with heterobifunctional dyes. The attachment reaction mechanisms between the reactive dyes, β-CD and cellulose fibre could be proposed to explain this result.

A β-CD molecule can only become anchored to the fibre if one of the reactive groups on the dye is able to react with one of its hydroxyl groups and the other with a hydroxyl group on cellulose, as illustrated in ***Figure 6***. It seems that an attachment reaction to the heterobifunctional reactive dye followed the reaction mechanism: Cell-O-Dye-O-Cell, β-CD-O-Dye-O-β-CD, Cell-O-Dye-O-β-CD-O-Dye-O-Cell. The fabric samples treated with heterobifunctional and β-CD show less intense colour compared to that of the homobifunctional reactive dye treated samples, demonstrating the above-mentioned three reaction mechanism.

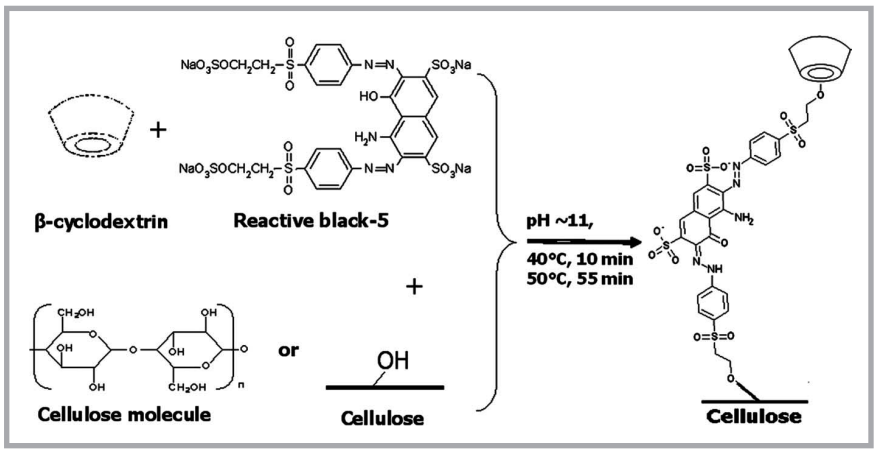

Figure 6. *Schematic representation of chemical modifying reaction of a homobifunctional reactive dye as the connector between β-CD and a cotton substrate [31].*

Modification with non-reactive CD by polymeric binders

Nano-composite dense polymer

The sol–gel method has become another technique to modify fibres by the hydrolysis and condensation of metal alkoxides, building a large metal-containing polymer network with a three-dimensional structure. In general, the sol-gel process was also applied for the modification of fibres by the pad-dry-cure method, which involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of a sol to form a network in a continuous liquid phase (gel). As precursors to preparing the sol, silicon alkoxides [Si(OR)4] are the most common starting compounds containing reactive alkoxide groups (–OR), which react readily with water in the hydrolysis reaction. The hydrolysis reaction replaces alkoxide groups with hydroxyl groups (–OH), which in the subsequent condensation reaction produce metaloxane bonds (M–O–M). Thus, in the pad-dry-cure method, a dense nanocomposite polymer film of 10 nm thickness is successfully formed on the fibre surface by hydrogen or covalent binding [32].

Fibres were modified with non-reactive CD by the sol-gel method in Wang's researches [33,34]. Tetraethyl orthosilicate (TEOS) and (3-Glycidoxypropyl) methyldiethoxysilane (GPTMS) were chosen as the precursor and coupling agent, respectively. TEOS makes a sol and forms a gel when crosslinked with GPTMS.

β-CD was dissolved before [33] or after [35] the sol-gel solution formed. The stability of the sol-gel solution decreased greatly in the presence of β-CD, due to the reaction between the OH group of β-CD and hydrolysed GPTMS. Then no more than 0.5 $mol \cdot l^{-1}$ β-CD was anchored on the fabric by the two different processes. The fabircs could be dipped and padded by sol containing β-CD and then treated by dyring and curing, or firstly dipped and padded by pure β-CD solution and then modified by the sol-gel process. As a result, the latter method was more feasible and beneficial to strengthen the binding between cyclodextrin and fibres, which improves the washing fastness of the treated fabric.

β-CD can also be cross-linked by means of a water-based organic solvent-free approach to nanogels with a high active β-CD content. Nanogels also show good adhesion to surfaces with a size of 25 nm under dry conditions [36]. Kettel [37] prepared nanogels in water by the cross-linking of β-CD with NCO-terminated star-shaped prepolymer on the basis of polyethylene oxide and polypropylene oxide. Wool textiles were dipped and padded with a dispersion containing nanogel particles, then dried at room temperature and further at 80 °C. The coating formed on the surface of the wool fabric was analysed by field emission electron microscopy. Agglomerations and dense distribution characterise the surface of the fabric.

Graft polymerisation of glycidyl methacrylate

Active polymer radicals generated by electric discharges initiate the graft polymerisation of a vinyl monomer, and a coating structure thereof can be formed on fibre surfaces. Glycidyl methacrylate (GMA) is widely used to form polymer coatings due to the pendant epoxy group, which can be chemically coupled with a functional group, such as the –OH of β-CD and natural fibres. The graft polymerisation of GMA can be achieved using different radical generation techniques, such as chemically initiation, photochemical initiation, plasma initiation, enzymatic initiation, linear electron beam radiation and gamma-rradiation [38-40]. Graft polymerisation can be performed using either pre-irradiation grafting or simultaneous(mutual) grafting.

Hirotsu [41] firstly pretreated cellulose fibres with glow discharge plasma to form active radicals that can initiate the graft polymerisation of GMA. And then the GMA-grafted fibre was modified with β-CD in NaCl water-dimethylformamide. The modification of cellulose fabrics with β-CD was confirmed by the mass increase in grafted fibre.

Linear electron beam radiation can also be used to induce the grafting of GMA/β-CD on cotton fabric. Fabrics were treated with a GMA or GMA/β-CD mixture and then irradiated with a linear electron beam accelerator to initiate a grafting reaction. The previously radiation-grafted cotton fabrics were retreated with β-CD solution containing NaCl and NaOH. Then modification of the GMA grafted cellulose fabrics was completed probably via the cleavage of the epoxide ring in the

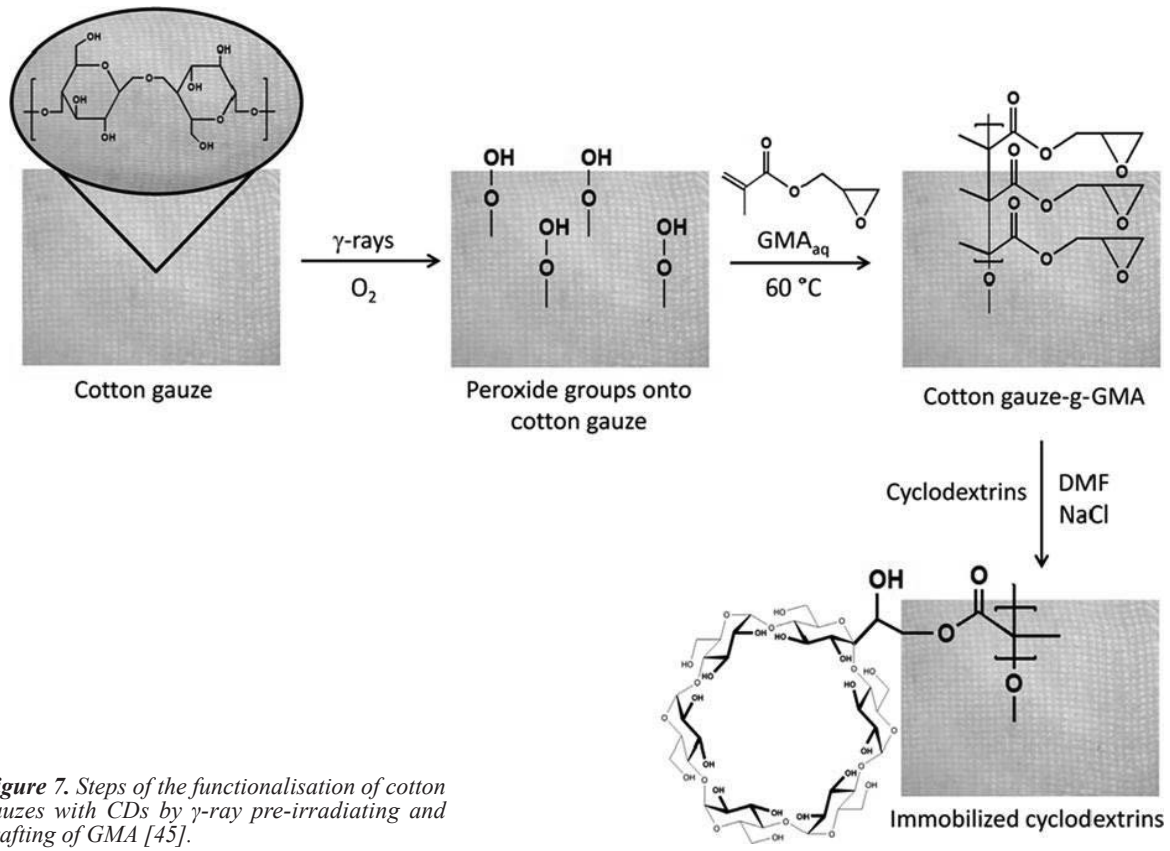

Figure 7. *Steps of the functionalisation of cotton gauzes with CDs by γ-ray pre-irradiating and grafting of GMA [45].*

GMA grafted cellulose fabrics with –OH in the β-CD molecule [42,43].

Desmet [44] functionalised cotton-cellulose by the gamma-irradiation-induced grafting of GMA to obtain a hydrophobic cellulose with epoxy groups suitable for further chemical modification. Two different grafting techniques were applied. In pre-irradiation grafting, cellulose was irradiated by $^{60}C_0$ γ-rays (absorbed dose: 2.5-40kGy, dose rate: 6kGy^{-1}) in air and then immersed in a GMA monomer solution, whereas in simultaneous grafting, cellulose was irradiated in an inert atmosphere in the presence of a monomer. Pre-irradiation led to a more homogeneous fibre surface and simultaneous grafting resulted in a higher grafting yield, but it showed clear indications of some GMA-homopolymerisation, due to the different grafting mechanisms (in simultaneous grafting technology grafting occurs mainly on the surface, while pre-irradiation grafting is more homogeneous throughout the cross-section). β-CD was added to the grafting solution and immobilised onto the cellulose during simultaneous irradiation. The mass increase upon grafting was higher than in comparable samples without β-CD added, indicating the incorporation of β-CD. γ-ray pre-irradiation grafting was also used to modify cotton gauzes with GMA groups, imparting β-CD covalently bound to the GMA functionalized gauzes (as shown in ***Figure 7***). Low irradiation doses (from 1 to 7.5 kGy) and relatively low GMA concentration (10% v/v) were chosen to prevent the degradation of cellulose chains and to avoid homopolymerisation [45].

Modification with reactive CD

Derivatives of CDs with a reactive group reacting with hydroxyl groups of cellulose were also applied for natural fabric modification [6, 46-49].

MCT-β-CD was used for cellulose functionalisation based on the coupling reaction between the chlorotriazine group of β-CD and nucleophilic surface groups as per conventional dyeing processes [50-52]. The chlorotriazine group can be introduced to the β-CD molecule according to the procedure described by Renscher and Hinsenkorn [49].

MCT-β-CD was applied in the modification of a cotton cellulose surface by the covalent binding of the chlorotriazine part of CD to cellulose hydroxyls. The pad-dry-cure process [53, 54] is the most common approach to modify cotton [55] or hemp [56] fabrics with MCT-β-CD in the presence of alkaline medium. The extent of the reaction was increased with the increased concentration of MCT-β-CD, due to the greater availability of MCT-β-CD in the proximity of the hydroxyl groups of cotton cellulose. Hydrolysis of the monochlorotriazinyl group was inevitable along with the covalent reaction. The nature and concentration of the catalyst also influenced the extent of the reaction [57, 58]. The best fixation of MCT-β-CD to cotton fabrics was achieved at higher temperature. And the reactivity of cotton fabrics were enhanced by initially dipping them in an aqueous solution of Na_2CO_3 and then leaving them to dry before the pad-dry-cure process [59].

The cationisation of cotton fabric also has a great effect on the covalent reaction efficiency. The results obtained revealed that cationised cellulose fabrics display higher reaction efficiency with MCT-β-CD than with MCT-β-CD pretreated cotton, followed by cationisation. The cationic groups in the precationized cotton fabric form an alkali site that might stimulate in-situ the reaction between MCT-β-CD and the pre-cationised cotton [60].

The permanent grafting of MCT-β-CD could also be carried out by dipping cotton samples in an aqueous solution of MCT-β-CD and sodium carbonate, followed by squeezing and treating at 130~150 °C to minimise the reaction of MCT-β-CD with air moisture [31, 61-65]. Biopolishing, a cellulose enzyme treatment, raised the grafting yield of MCT-β-CD remarkably [66].

Another comparable fixation uses a third molecule as a kind of intermediate between fibre and cyclodextrin. These compounds react with both the hydroxyl groups of cyclodextrins and textile fibre functional groups e.g., cellulose hydroxyls. Furthermore, some network formation takes place, which leads to a combined fixation and the entrapment of cyclodextrins [67].

So as to introduce a permanent softening effect on cotton fabric, butyl acrylate (BuA) was selected to be graft polymerised with MCT-β-CD. Cotton fabrics were in situ grafted with MCT-β-CD as well as BuA using a potassium persulphate/ammonium persulphate mixture as the initiatior, or grafted with the reactive preformed polymer: MCT-β-CD grafted with poly (BuA). Despite the great differences in graft yield and grafting efficiency found between the modified cotton processed as per the first approach and those of the second approach, the two approaches succeeded in producing modified cottons with BuA moieties along with RCD moieties [68].

Grafting the reactive preformed polymer, MCT-β-CD grafted with poly(BuA), onto fabric was better achieved when applied with epichlorohydrin due to crosslinks between the reactive preformed polymer and epichlorohydrin. In other words, the reactive preformed polymer is grafted to cotton in the absence of epichlorohydrin only through a substitution reaction involving the monochlorotriazinyl group of the reactive preformed polymer and the cotton hydroxyls. In the presence of epichlorohydrin, on the other hand, extra chemical bonding resulting from the reaction of it with the hydroxyl groups of both the reactive preformed polymer and cotton will come to play. Needless to say that such extra chemical bonding will be associated with the additional amount of reactive preformed polymer chemically attached to the cotton [69].

MCT-β-CD can also be anchored to cotton fabrics through chemical bonding during the grafting of bifunctional glycidyl methacrylate(GMA) monomers onto cotton. The grafting of GMA onto cotton cellulose involves the following three steps: (1) the abstraction of hydrogen atoms from cellulose by radiation leads to the formation of cellulose macro radicals; (2) grafting occurs via the additional bond of the monomer in the presence of a GMA monomer, and (3) subsequent addition of monomer molecules. Cotton fabrics were firstly completely immersed in a GMA or GMA/MCT-β-CD bath, followed by squeezing, irradiating and washing. Then the cotton fabrics grafted with GMA or GMA/MCT-β-CD were retreated in a solution containing MCT-β-CD, NaCl and NaOH at 80 °C for 1 h [70, 71]. MCT-β-CD anchoring to Cell-g-GMA occured most probably via the monochloro triazinyl group. It exhibited add-on values which increase as the radiation dose increases, which indicated that the adverse effect of higher radiation doses is offset, and instead the favorable effect on the fixed MCT-β-CD is continued up to a radiation dose of 5x10 KGy. The presence of a monochloro triazinyl group as part of the MCT-β-CD molecule seems to counterbalance the degradative action of radiation even when employed at a dose as high as 5x10 KGy [71].

Conclusions

Natural fibres have been widely applied as suitable matrix in preparing functional materials containing CDs. To form functional structures and satisfy the fastness desired, natural fibres have been modified with a permanent finishing effect by a multiplicity of grafting modification techniques. In different reserches various crosslinking chemicals such as DMDHEU, butane tetracarboxylic acid, citric acid, maleic anhydrides, polyaminocarboxylic acids, glyoxal, epichlorohydrin and bifunctional reactive dyes were chosen to bind cyclodextrin with natural fibres. The grafting modication based on these crosslinking chemicals should balance the drawbacks with the grafting effect , drawbacks which include formaldehyde release, strength loss and yellowing of the treated fabrics. Low temperature oxygen plasma was used to improve the absorption of cyclodextrin on natural fibres. Dense nanocomposite polymer film could also be formed to anchor cyclodextrin on a natural fibre surface by the pad-dry-cure method due to hydrogen binding or covalent binding in the sol-gel process. Natural fabrics could be treated by sol containing β-CD or by firstly being dipped in and padded by pure β-CD solution and then modified by the sol-gel process. The latter method was more feasible and beneficial to strengthen the binding between cyclodextrin and fibres, which improves the washing fastness of the treated fabric. Graft polymerisation of vinyl monomer can be performed using either pre-irradiation grafting or simultaneous (mutual) grafting to form a polymer coating, imparting cyclodextrins covalently bound to the functionalised fabrics. Derivatives of CDs with a reactive group such as a chlorotriazine group were also applied for natural fabric modification. The cationisation of cotton fabric and use of a crosslinking agent have a great effect on the covalent reaction efficiency. Reactive CDs can also be anchored to natural fibres through chemical bonding during the grafting of bifunctional monomers onto fibres. These grafting modification techniques were successfully applied to combine natural fibres with the capacity of cyclodextrins to form inclusion complexes with various special properties.

Declaration of conflicting interests

The Authors declare no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

Acknowledgements

This work was supported by the Natural Science Foundation of the Shaanxi Provincial Department of Education [grant number 19JK0362], by the Science and Technology Guidance Project of China National Textile and Apparel Council [grant number 2019040], and by PhD Research Funds of Xi'an Polytechnic University [grant number BS1721].

References

1. Wong CE, Dolzhenko AV, Lee SM, et al. Cyclodextrins: A Weapon in the Fight Against Antimicrobial Resistance. *Journal of Molecular Engineering Materials* 2017; 5(01):1740006.
2. Ghorani B, Kadkhodaee R, Rajabzadeh G, et al. Assembly of Odour Adsorbent Nanofilters by Incorporating Cyclodextrin Molecules into Electrospun Cellulose Acetate Webs. *Reactive Functional Polymers* 2019; 134: 121-132.
3. Morin-Crini N, Winterton P, Fourmentin S, et al. Water-Insoluble B-Cyclodextrin–Epichlorohydrin Polymers for

Removal of Pollutants from Aqueous Solutions by Sorption Processes Using Batch Studies: A Review of Inclusion Mechanisms. *Progress in Polymer Science* 2018;78:1-23.
4. Ishiguro T, Sakata Y, Arima H, et al. Release Control of Fragrances by Complexation with B-Cyclodextrin and Its Derivatives. *Journal of Inclusion Phenomena Macrocyclic Chemistry* 2018; 92(1-2): 147-155.
5. Marcos X, Pérez-Casas S, Llovo J, et al. Poloxamer-Hydroxyethyl Cellulose -A-Cyclodextrin Supramolecular Gels for Sustained Release of Griseofulvin. *International Journal of Pharmaceutics* 2016; 500(1-2):11-19.
6. Cova TF, Murtinho D, Pais AA, et al. Combining Cellulose and Cyclodextrins: Fascinating Designs for Materials and Pharmaceutics. *Frontiers in Chemistry* 2018; 6: 271.
7. Del Valle EM. Cyclodextrins and their Uses: A Review. *Process Biochemistry* 2004; 39(9): 1033-1046.
8. Hedges AR. Industrial Applications of Cyclodextrins. *Chemical Reviews* 1998; 98(5): 2035-2044.
9. Irie T, Uekama K. Pharmaceutical Applications of Cyclodextrins. III. Toxicological Issues and Safety Evaluation. *Journal of Pharmaceutical Sciences* 1997; 86(2): 147-162.
10. Loftsson T, Brewster ME. Pharmaceutical Applications of Cyclodextrins. 1. Drug Solubilization and Stabilization. *Journal of Pharmaceutical Sciences* 1996; 85(10): 1017-1025.
11. Li B, Dong Y, Wang P, et al. Release Behavior and Kinetic Evaluation of Formaldehyde from Cotton Clothing Fabrics Finished with DMDHEU-Based Durable Press Agents in Water and Synthetic Sweat Solution. *Textile Research Journal* 2016; 86(16): 1738-1749.
12. Montazer M, Mehr EB. Na-Diclofenac B-Cyclodextrin Inclusion Complex on Cotton Wound Dressing. *Journal of the Textile Institute* 2010; 101(5): 373-379.
13. Hong KH. Preparation and Properties of Phenolic Compound/BTCA Treated Cotton Fabrics for Functional Textile Applications. *Cellulose* 2015; 22(3): 2129-2136.
14. Voncina B, Le Marechal AM. Grafting of Cotton with B-Cyclodextrin via Poly (Carboxylic Acid). *Journal of Applied Polymer Science* 2005; 96(4): 1323-1328.
15. Medronho B, Andrade R, Vivod V, et al. Cyclodextrin-Grafted Cellulose: Physico -Chemical Characterization. *Carbohydrate Polymers* 2013; 93(1): 324-330.
16. Novikov M, Thong KL, Zazali NIM, et al. Treatment of Cotton by β-Cyclodextrin/ Triclosan Inclusion Complex and Factors Affecting Antimicrobial Properties. *Fibers and Polymers* 2018; 19(3): 548-560.
17. El-Tahlawy K, El-Nagar K, Elhendawy A. Cyclodextrin-4 Hydroxy Benzophenone Inclusion Complex for UV Protective Cotton Fabric. *Journal of the Textile Institute* 2007; 98(5): 453-462.
18. Bajpai M, Gupta P, Bajpai S. Silver (I) Ions Loaded Cyclodextrin-Grafted-Cotton Fabric with Excellent Antimicrobial Property. *Fibers and Polymers* 2010; 11(1): 8-13.
19. Salah F, El Ghoul Y, Roudesli S. Bacteriological Effects of Functionalized Cotton Dressings. *Journal of the Textile Institute* 2016; 107(2): 171-181.
20. Gawish S, Ramadan A, Abo El-Ola S, et al. Citric Acid used as a Cross-Linking Agent for Grafting B-Cyclodextrin onto Wool Fabric. *Polymer-Plastics Technology Engineering* 2009; 48(7): 701-710.
21. Haji A, Mehrizi MK, Akbarpour R. Optimization of B-Cyclodextrin Grafting on Wool Fibers Improved by Plasma Treatment and Assessment of Antibacterial Activity of Berberine Finished Fabric. *Journal of Inclusion Phenomena* 2015; 81(1-2): 121-133.
22. Mehraz L, Nouri M. Preparation and Characterization of B-Cyclodextrin Grafted Silk Fabric. *Journal of Natural Fibers* 2018: 1-11.
23. Bandyopadyay S, Das D. Retention and Sustained Release of Fragrance by Cyclodextrin Functionalized Cotton Fabric Modified using Maleic Anhydride. *Flavour Fragrance Journal* 2017; 32(3): 207-211.
24. Dehabadi VA, Buschmann H-J, Gutmann JS. A Novel Approach for Fixation of B-Cyclodextrin on Cotton Fabrics. *Journal of Inclusion Phenomena Macrocyclic Chemistry* 2014; 79(3-4): 459-464.
25. Hebeish A, Sharaf S, Refaie R, et al. Multifinishing of Cotton Fabrics using Microwave Techniques. *Research Journal of Textile Apparel* 2012; 16(2): 68-81.
26. Ping Z, Xin Y, Lin Z, et al. Study on Inclusion Medicine of Cotton Fabric Grafted with B-Cyclodextrin. *Journal of Textile Research* 2010; 31(7): 64-68.
27. Youyi X, Junmin W. Preparation and Mechanism of B-Cycldextrin Grafted Cellulose Fiber. *Journal of Textile Research* 2006; 27(2): 25-28.
28. Szejtli J, Zsadon B, Fenyvesi E, et al. Sorbents of Cellulose Basis Capable of Forming Inclusion Complexes and a Process for the Preparation Thereof. U.S. Patent 4,357,468. 1982-11-2.
29. Neto R, Cardoso A, Silva C. Functional Substrates for the Gradual Release of Agents. *Progress in Organic Coatings* 2015; 78: 474-479.
30. Wang C X, Chen S L. Anchoring B-Cyclodextrin to Retain Fragrances on Cotton by Means of Heterobifunctional Reactive Dyes. *Coloration Technology* 2004; 120(1): 14-18.
31. Agrawal P, Warmoeskerken M. Permanent Fixation of B-Cyclodextrin on Cotton Surface-an Assessment between Innovative and Established Approaches. *Journal of Applied Polymer Science* 2012; 124(5): 4090-4097.
32. Ismail WNW. Sol-Gel Technology for Innovative Fabric Finishing-A Review. *Journal of Sol-Gel Science Technology* 2016; 78(3): 698-707.
33. Wang C X, Chen S L. Surface Treatment of Cotton Using B-Cyclodextrins Sol-Gel Method. *Applied Surface Science* 2006; 252(18): 6348-6352.
34. Wang C X, Chen S L. Surface Modification of Fabric by Sol-Gel Method. *Journal of Textile Research* 2005; 26(4): 24.
35. Ghosh S, Chipot N. Embedding Aromatherapy Essential Oils into Textile Fabric using B-Cyclodextrin Inclusion Compound. *Indian Journal of Fibre & Textile Research* 2015; 40: 140-143.
36. Kettel MJ, Hildebrandt H, Schaefer K, et al. Tenside-Free Preparation of Nanogels with High Functional B-Cyclodextrin Content. *ACS nano* 2012; 6(9): 8087-8093.
37. Kettel MJ, Schaefer K, Groll J, et al. Nanogels with High Active B-Cyclodextrin Content as Physical Coating System with Sustained Release Properties. *ACS Applied Materials Interfaces* 2014; 6(4): 2300-2311.
38. Madrid JF, Abad LV. Modification of Microcrystalline Cellulose by Gamma Radiation-Induced Grafting. *Radiation Physics Chemistry* 2015; 115: 143-147.
39. Madrid JF, Nuesca GM, Abad LV. Gamma Radiation-Induced Grafting of Glycidyl Methacrylate (GMA) onto Water Hyacinth Fibers. *Radiation Physics Chemistry* 2013; 85: 182-188.
40. Wojnárovits L, Földváry CM, Takács E. Radiation-Induced Grafting of Cellulose for Adsorption of Hazardous Water Pollutants: A Review. *Radiation Physics Chemistry* 2010; 79(8): 848-862.
41. Hirotsu T. Plasma Graft Polymerization of Glycidyl Methacrylate and Cyclodextrin Immobilization. *Thin Solid Films* 2006; 506: 173-175.
42. Abdel-Halim E, Fouda MM, Hamdy I, et al. Incorporation of Chlorohexidin Diacetate into Cotton Fabrics Grafted with Glycidyl Methacrylate and Cyclodextrin. *Carbohydrate Polymers* 2010; 79(1): 47-53.
43. Hebeish A, El-Sawy S, Ragaei M, et al. New Textiles of Biocidal Activity by Introduce Insecticide in Cotton-Poly (GMA) Copolymer Containing B-Cd. *Carbohydrate Polymers* 2014; 99: 208-217.
44. Desmet G, Takács E, Wojnárovits L, et al. Cellulose Functionalization via High -Energy Irradiation-Initiated Grafting of Glycidyl Methacrylate and Cyclodextrin Immobilization. *Radiation Physics Chemistry* 2011; 80(12): 1358-1362.
45. Hiriart-Ramírez E, Contreras-García A, Garcia-Fernandez MJ, et al. Radiation Grafting of Glycidyl Methacrylate onto Cotton Gauzes for Functionalization with Cyclodextrins and Elution of Antimicrobial Agents. *Cellulose* 2012; 19(6): 2165-2177.
46. Denter U, Schollmeyer E. Surface Modification of Synthetic and Natural Fibres

by Fixation of Cyclodextrin Derivatives. *Proceedings of the Eighth International Symposium on Cyclodextrins*. Springer, Dordrecht, 1996: 559-564.
47. Lee MH, Yoon KJ, Ko SW. Synthesis of a Vinyl Monomer Containing B-Cyclodextrin and Grafting onto Cotton Fiber. *Journal of Applied Polymer Science* 2001; 80(3): 438-446.
48. Nostro PL, Fratoni L, Baglioni P. Modification of a Cellulosic Fabric with B-Cyclodextrin for Textile Finishing Applications. *Journal of Inclusion Phenomena Macrocyclic Chemistry* 2002; 44(1-4): 423-427.
49. Reuscher H, Hirsenkorn R. BETA W7 MCT-New Ways in Surface Modification. *Proceedings of the Eighth International Symposium on Cyclodextrins*. Springer, Dordrecht, 1996: 553-558.
50. Buschmann H, Knittel D, Schollmeyer E. Use of Cyclodextrin±Dye Complexes in Dyeing Processes. *Textilveredlung* 1996; 31: 115-117.
51. Peila R, Migliavacca G, Aimone F, et al. A Comparison of Analytical Methods for the Quantification of a Reactive B-Cyclodextrin Fixed onto Cotton Yarns. *Cellulose* 2012; 19(4): 1097-1105.
52. Xiao Z, Feng N, Zhu G, et al. Preparation and Application of Citral–Monochlorotriazine-B-Cyclodextrin Inclusion Complex Nanocapsule. *Journal of The Textile Institute* 2016; 107(1): 64-71.
53. Hebeish A, Fouda MM, Hamdy I, et al. Preparation of Durable Insect Repellent Cotton Fabric: Limonene as Insecticide. *Carbohydrate Polymers* 2008;74(2): 268-273.
54. Shahba AF. Production and Characterization of Novel Perfumed Curtain Fabrics. *Research Journal of Textile Apparel* 2008; 12(4): 31-40.
55. Angela C, Luminita C, Muresan E, et al. Textile Materials Functionalised with Natural Biologically Active Compounds. *Romanian Biotechnological Letters* 2010; 15(5): 5538.
56. Racu C, Cogeanu AM, Diaconescu RM, et al. Antimicrobial Treatments of Hemp Fibers Grafted with B-Cyclodextrin Derivatives. *Textile Research Journal* 2012; 82(13): 1317-1328.
57. Hebeish A, El-Hilw Z. Chemical Finishing of Cotton using Reactive Cyclodextrin. *Coloration Technology* 2001; 117(2): 104-110.
58. Kistamah N, Carr C, Rosunee S. Surface Chemical Analysis of Tencel and Cotton Treated with a Monochlorotriazinyl (MCT) B-Cyclodextrin Derivative. *Journal of Materials Science* 2006; 41(8): 2195-2200.
59. Sricharussin W, Sopajaree C, Maneerung T, et al. Modification of Cotton Fabrics with B-Cyclodextrin Derivative for Aroma Finishing. *Journal of the Textile Institute* 2009; 100(8): 682-687.
60. Hashem M, El-Aref A, Refaie R. Cotton Fabric Bearing Cationic and B-Cyclodextrin Moieties: A Study of the Reaction Parameters. *Research Journal of Textile* 2004; 8(2): 76-94.
61. Abdel-Mohdy F, El-Aref A, Hashem A, et al. Monochlorotriazinyl-cyclodextrin Finished Cotton Fabric and Its Inclusion Ability Towards Some Guest Molecules. *Egyptian Journal of Textile Polymer Science Technology* 2005; 9(2): 85-95.
62. Abdel-Mohdy F, Fouda MM, Rehan M, et al. Repellency of Controlled-Release Treated Cotton Fabrics Based on Cypermethrin and Prallethrin. *Carbohydrate Polymers* 2008; 73(1): 92-97.
63. Chen M, Wang Y, Xie X, et al. Inclusion Complex of Monochlorotriazine-Beta-Cyclodextrin and Wormwood oil: Preparation, Characterization, and Finishing on Cotton Fabric. *The Journal of The Textile Institute* 2015; 106(1): 31-38.
64. Setthayanond J, Sodsangchan C, Suwanruji P, et al. Influence of MCT-B-Cyclodextrin Treatment on Strength, Reactive Dyeing and third-hand Cigarette Smoke Odor Release Properties of Cotton Fabric. *Cellulose* 2017; 24(11): 5233-5250.
65. Sodsangchan C, Setthayanond J, Suwanruji P. Influence of Monochlorotriazine-B-Cyclodextrin Treatment on Dyeing and Fastness Properties of the Hot-Dyeing Reactive Dye on Cotton. Paper presented at: *Applied Mechanics and Materials*, 2014.
66. Sundrarajan M, Rukmani A. Biopolishing and Cyclodextrin Derivative Grafting on Cellulosic Fabric for Incorporation of Antibacterial Agent Thymol. *Journal of the Textile Institute* 2013; 104(2): 188-196.
67. Kut D, Gunesoglu C, Orhan M. An investigation into the possibility of using cyclodextrin in crease resistant finish. *FIBRES &TEXTILES in Eastern Europe* 2007, 15, 2(61): 93-96.
68. Hebeish A, El Shafei A, Shaarawy S. Synthesis and Characterization of Multifunctional Cotton Containing Cyclodextrin and Butylacrylate Moieties. *Polymer-Plastics Technology Engineering* 2009; 48(8): 839-850.
69. El Shafei A, Shaarawy S, Hebeish A. Application of Reactive Cyclodextrin Poly Butyl Acrylate Preformed Polymers Containing Nano-Zno to Cotton Fabrics and their Impact on Fabric Performance. *Carbohydrate Polymers* 2010; 79(4): 852-857.
70. Abdel-Halim E, Abdel-Mohdy F, Fouda MM, et al. Antimicrobial Activity of Monochlorotriazinyl-B-Cyclodextrin/Chlorohexidin Diacetate Finished Cotton Fabrics. *Carbohydrate Polymers* 2011; 86(3): 1389-1394.
71. Hebeish AA, Abdel-Halim ES, Hamdy IA, et al. Synthesis of Cotton Graft Copolymers Containing Glycidyl Methacrylate and Different Cyclodextrins Moieties Using Linear Electron Beam Radiation. *Research Journal of Textile Apparel* 2009; 13(3): 57-68.

Received 09.10.2019 Reviewed 16.04.2020