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# Cyclodextrins in Textile Finishing

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Additional information is available at the end of the chapter

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## 1. Introduction

Chemical finishing is crucial for giving textiles new functionalities and making them appropriate for special applications, such as antimicrobial resistance, flame retardancy and others. Textile finishing is also an important process as it improves appearance, performance or hand.

Cyclodextrins can act as hosts and form inclusion compounds with various small molecules. Such complexes can be formed in solutions, in a solid state as well as when cyclodextrins are linked to various surfaces where they can act as permanent or temporary hosts for small molecules that provide certain desirable attributes. This characteristic makes cyclodextrin a promising reagent in textile finishing.

## 2. Cyclodextrins

Cyclodextrins(CDs) are relevant molecules used in different applications and industries from pharmacology, cosmetics, textiles, filtration to pesticide formulations. They comprise a family of three well-known industrially produced substances. The practically important, industrially produced CDs are the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CDs. There are some seldom used cyclic oligosaccharides as well but because of their cost are not applicable to industrial applications [1]. CDs are cyclic oligomers of  $\alpha$ -D-glucopyranose that can be produced with the transformation of starch by certain bacteria such as *Bacillus macerans* [2, 3].

The preparation process of CDs consists of four principal phases: (i) culturing of the microorganism that produces the cyclodextrin glucosyl transferase enzyme (CGT-ase); (ii) separation, concentration and purification of the enzyme from the fermentation medium; (iii) enzymatical conversion of prehydrolyzed starch in mixture of cyclic and acyclic dextrins;

and (iv) separation of CDs from the mixture, their purification and crystallization. CGT-ase enzymes degrade the starch and starts intramolecular reactions without the water participation. In the process, cyclic (CDs) and acyclic dextrins are originated, which are oligosaccharides of intermediate size. CDs are formed by the link between units of glucopyranose. The union is made through glycosidic oxygen bridges by  $\alpha$ -(1,4) bonds. The purification of  $\alpha$ - and  $\gamma$ -CDs increases the cost of production considerably, so that 97% of the CDs used in the market are  $\beta$ -CDs [2].

CDs ring structures act as hosts and form inclusion compounds with various small molecules. Such complexes can be formed in solutions, in a solid state as well as when cyclodextrins are linked to various surfaces. In all forms they can act as permanent or temporary hosts to small molecules that provide certain desirable attributes.

In the textile field CDs may have many applications such as: absorption of unpleasant odours; they can complex and release fragrances, “skin-care-active” and bioactive substances. Further, various textile materials treated with cyclodextrins could be used as selective filters for adsorption of small pollutants from waste water [4].

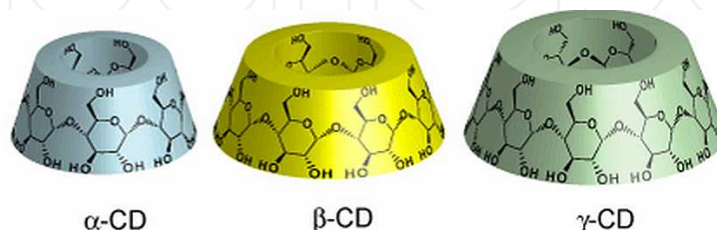
After the discovery of CDs scientists considered them poisonous substances and their ability for complexes formation was only considered a scientific curiosity. Later on, research on CDs proved that they are not only non-toxic but they can be helpful for protecting flavours, vitamins and natural colours [2]. CDs already play a significant role in the textile industry and can be used in dyeing, surface modification, encapsulation, washing, and preparation of polymers and in fibre spinning.

Since year 2000,  $\beta$ -CD has been introduced as a food additive in Germany. With respect to OECD experiments, this compound has shown no allergic impact. In the USA  $\alpha$ -,  $\beta$ - and  $\gamma$ -CDs have obtained the GRAS list (FDA list of food additives that are ‘generally recognized as safe’) status and can be commercialized as such. In Japan  $\alpha$ -,  $\beta$ - and  $\gamma$ -CDs are recognized as natural products and their commercialization in the food sector is restricted only by considerations of purity. In Australia and New Zealand  $\alpha$ - and  $\gamma$ -CDs are classified as Novel Foods from 2003 and 2004, respectively. The recommendation of Joint FAO/WHO Expert Committee on Food Additives (JECFA) for a maximum level of  $\beta$ -CDs in foods is 5 mg/kg per day. For  $\alpha$ - and  $\gamma$ -CDs no Acceptable Daily Intake (ADI) was defined because of their favourable toxicological profiles [2, 5].

Natural cyclodextrins and their hydrophilic derivatives are only able to permeate lipophilic biological membranes, such as the eye cornea, with considerable difficulty. All toxicity studies have demonstrated that orally administered cyclodextrins are practically non-toxic, due to lack of absorption from the gastrointestinal tract. The main properties of  $\beta$ -CD, the most important cyclodextrin in textile application are: less irritating than  $\alpha$ -CD after i.m. injection, binds cholesterol, small amount (1-2%) is adsorbed in the upper intestinal tract, no metabolism in the upper intestinal tract, metabolised by bacteria in caecum and colon, LD50 oral rat > 5000 mg/kg, LD50 i.v., rat: between 450-790 mg/kg, however, application of high doses may be harmful and is not recommended [6, 7].

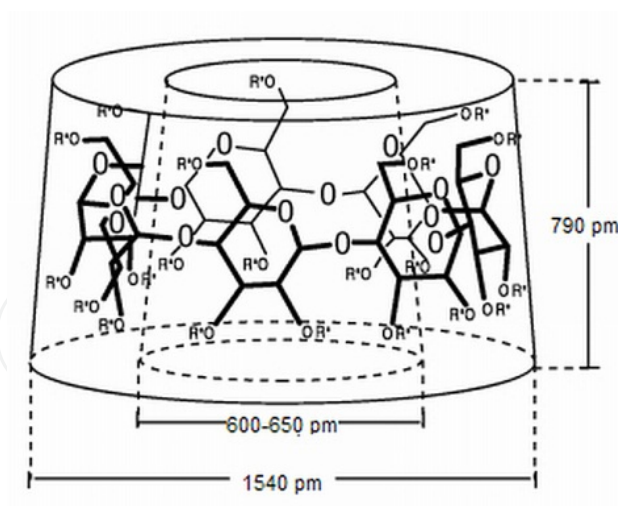
## 2.1. Structure of cyclodextrins

The three major CDs are crystalline, homogeneous, and non-hygroscopic substances, which are torus-shaped oligosaccharides [1, 8-10], composed in the more common forms of six to eight ( $\alpha$ -1,4)-linked  $\alpha$ -D-glucopyranose units ( $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrin), Figure 1 schematically present the main three cyclodextrins [11]. They are of circular and conical conformation, where the height is about 800 pm. The inner diameter of the cavity varies from 500 to 800 pm.



**Figure 1.** Schematic presentation of the main three CDs [12].

All glucopyranose units in the torus-like ring possess the thermodynamically favoured chair conformation because all substituents are in the equatorial position. As a consequence of the  $4C_1$  conformation of the glucopyranose units, all secondary hydroxyl groups are situated on the larger side of the ring, whereas all the primary ones are placed on the narrower side of the ring. Hydroxyl groups on the outside of the CDs ensure good water solubility. The cavity is lined with hydrogen atoms of C3, by the glycosidic oxygen bridges and hydrogen atoms of C5. The nonbonding electron pairs of the glycosidic oxygen bridges are directed toward the inside of the cavity producing a high electron density and because of this the inner side of the cavity has some Lewis base characteristics. The C-2-OH group of one glucopyranoside unit can form a hydrogen bond with the C-3-OH group of the adjacent glucopyranose unit. In the CD molecule, a complete secondary belt is formed by these hydrogen bonds, therefore the  $\beta$ -CD has a rather rigid structure. Because of this arrangement, the interior of the toroids is not hydrophobic but considerably less hydrophilic than the aqueous environment and thus able to host other hydrophobic molecules. CDs behave more or less like rigid compounds with two degrees of freedom, rotation at the glucosidic links C4-O4 and C1-O4 and rotations at the O6 primary hydroxyl groups at the C5-C6 band. The intramolecular hydrogen bond formation is probably the explanation for the observation that  $\beta$ -CD has the lowest water solubility of all CDs. The hydrogen-bond belt is incomplete in the  $\alpha$ -CD molecule, because one glucopyranose unit is in a distorted position. Consequently, instead of the six possible H-bonds, only four can be established fully.  $\gamma$ -CD is a noncoplanar with more flexible structure; therefore, it is the most soluble of the three CDs. Figure 2 shows a sketch of the characteristic structural features of CDs. On the side where the secondary hydroxyl groups are situated, the diameter of the cavity is larger than on the side with the primary hydroxyls, since free rotation of the primary hydroxyls reduces the effective diameter of the cavity [13, 14].



**Figure 2.** Schematic presentations of characteristic structural features of CDs.

By far,  $\beta$ -cyclodextrin ( $\beta$ -CD), with 7 sugar units, has been commercially the most attractive (more than 95% consumed) due to its simple synthesis, availability and price.

A  $\beta$ -CD molecule has a molecular weight of 1135 and a height of 750–800 pm. The internal diameter of the molecule's hole is between 600 and 680 pm, and the external diameter is 1530 pm [1, 15]. The volume of the hole is 260–265 Å<sup>3</sup>, and the dissolution is 1.85 g/100 mL of water. The cavity is hydrophobic; the external section is hydrophilic in nature.  $\beta$ -CD is stable in alkali solutions and it is sensitive to acid hydrolysis [16].

## 2.2. Properties of cyclodextrins

The most notable feature of CDs is their ability to form solid inclusion complexes ("host-guest" complexes) with a very wide range of solid, liquid and gaseous compounds by a molecular complexation. The phenomenon of CD inclusion compound formation is a complicated process involving many factors playing an important role.

Complex formation is a dimensional fit between host cavity and guest molecule. The lipophilic cavity of CD molecules provides a microenvironment into which appropriately sized non-polar moieties can enter to form inclusion complexes. No covalent bonds are broken or formed during formation of the inclusion complex.

According to some authors [11, 17] hydrophobic interactions are the main driving forces for CD-based host-guest compounds. Other requirements such as steric hindrance and relation between sizes of host and guest cavities are also important. This is illustrated by the fact that not only hydrophobic interaction will lead to an association between a guest molecule and a CD but ionic solutes, such as non-associated inorganic salts, can also be involved in these complexes.

Some researchers [7] claim that the main driving force of complex formation is the release of enthalpy-rich water molecules from the cavity. The water molecules located inside the cavity cannot satisfy their hydrogen bonding potentials and therefore are of higher enthalpy.

The energy of the system is lowered when these enthalpy-rich water molecules are replaced with suitable guest molecules which are less polar than water. In an aqueous solution, the slightly apolar CD cavity is occupied by water molecules which are energetically unfavoured, and therefore can be readily substituted by appropriate "guest molecules" which are less polar than water. This apolar-apolar association decreases the CD ring strain resulting in a more stable lower energy state. The dissolved CD is the "host" molecule, and the "driving force" of the complex formation is the substitution of the high-enthalpy water molecules by an appropriate "guest" molecule.

The binding of guest molecules within the host CD is not fixed or permanent but rather is a dynamic equilibrium. Binding strength depends on how well the 'host-guest' complex fits together and on specific local interactions between surface atoms. Complexes can be formed either in solution or in the crystalline state and water is typically the solvent of choice. Inclusion complexation can be accomplished in a co-solvent system and in the presence of any non-aqueous solvent [7]. Generally, one guest molecule is included in one CD molecule, although in the case of some low molecular weight molecules, more than one guest molecule may fit into the cavity, and in the case of some high molecular weight molecules, more than one CD molecules may bind to the guest. In principle, only a portion of the molecule must fit into the cavity to form a complex. CD inclusion is a stoichiometric molecular phenomenon in which usually only one guest molecule interacts with the cavity of the CD molecules to become entrapped. 1:1 complex is the simplest and most frequent case. However, 2:1, 1:2, 2:2, or even more complicated associations, and higher order equilibrium exist almost always simultaneously.

Inclusion in CDs has a profound effect on the physicochemical properties of guest molecules as they are temporarily included within the host cavity.

These properties are:

- solubility enhancement of highly insoluble guests,
- stabilisation of labile guests against the degradative effects of oxidation, visible or UV light and heat,
- control of volatility and sublimation,
- physical isolation of incompatible compounds,
- chromatographic separations,
- taste modification by masking of flavours, unpleasant odours,
- controlled release of drugs and flavours,
- removal of dyes and auxiliaries from dyeing effluents,
- retarding effect in dyeing and finishing,
- protection of dyes from undesired aggregation and adsorption.



### 2.3. Application of cyclodextrins

Complexes can be formed in solutions, in the solid state, as well as when CDs are linked to a solid surface where they can act as permanent or temporary hosts to those small molecules that provide certain desirable attributes such as adsorption of dyestuff molecules, fragrances or antimicrobial agents. This "molecular encapsulation" is already widely utilized in many industrial products, technologies, and analytical methods [7, 18].

Due to the relatively non-polar character of the cavity in comparison to the polar exterior, CD can form inclusion complexes with a wide variety of guest molecules, such as drugs [19, 20, 21], ionic and non-ionic surfactants [23, 24, 25], dyes [26, 27] and polymers [28], etc. The use of CDs has increased annually around 20–30%, of which 80–90% was in food products [29]. In the pharmaceutical industry, CDs and their derivatives have been used either for complexation of drugs or as auxiliary additives such as solubilizers, diluents, or ingredients for improving of drugs physical and chemical properties, or to enhance the bioavailability of poorly soluble moieties [30]. In the chemical industry, CDs and their derivatives are used as catalysts to improve the selectivity of reactions, as well as for the separation and purification of industrial-scale products [31]. In the food, cosmetics, toiletry, and tobacco industries, CDs have been widely used either for stabilization of flavours and fragrances or for the elimination of undesired tastes, microbiological contaminations, and other undesired compounds [7]. For the last 30 years, the use of CDs and their derivatives in the textile domains has captivated a lot of attention. Many of the papers and patents report the use of CDs for finishing and dyeing processes. For instance, they discuss the capture of unpleasant smells due to perspiration, or how to do the controlled release of perfumes, insecticides and antibacterial agents [4, 32–45].

## 3. Cyclodextrins in textiles

In the textile field CDs may have many applications such as: they can absorb unpleasant odours; they can complex and release fragrances or "skin-care-active" substances like vitamins, caffeine and menthol as well as bioactive substances such as biocides and insecticides. Further, various textile materials treated with CDs could be used as selective filters for adsorption of small pollutants from waste waters - "preparation of textile nanosponges".

### 3.1. Cyclodextrins in textile finishing

One of the new concepts for modification of textile substrates is based on the permanent fixation of supramolecular compounds on the material's surface and, thus, imparts new functionality to the fabric. [46]. One of the most promising supramolecular moieties applied to textiles are CDs. Covalent bonding of CDs onto textile fibres was firstly patented in 1980 by Szejtli [47]. He and co-workers reported to bond CD via crosslinking reagent epichlorohydrin onto alkali-swollen cellulose fibres. They found out that CD covalently bonded to cellulose retained the ability to form complexes; when cellulose was treated with a drug it complexed with CD. The complexed drug was upon the contact with the skin released; cellulose textile

substrate containing covalently bound  $\beta$ -CD was treated with solution of iodine, potassium iodide and methanol as a solvent to prepare a medical bandage [48].

Szejtli published [4] a very extensive review about CDs in the textile industry. In his review he divided the application of CDs in textile sectors in the following areas: binding of CDs to fibre surfaces, CDs in textile dyeing, in textile finishing, CDs and detergents and miscellaneous applications of CDs in textile industry and textile care. Due to the fact that application of CDs in textile dyeing processes was extensively reported in a chapter of the book edited by Hauser [18], we will emphasis in current publication about the application of CDs in textile finishing.

### *3.1.1. Binding of cyclodextrins to fibre surfaces*

The attachment of CD molecules on textile substrate provides hosting cavities that can include a large variety of guest molecules for specific functionality. There are two possible approaches to bond CDs onto textile fibres such as chemical bonding of modified CDs on the fibre surfaces or to use bifunctional reagents to link CDs covalently on fibre surfaces.

The most promising approach to bond modified CDs onto textile fibres is the modification of CDs with trichlorotriazines to prepare monochlorotriazinyl-cyclodextrin (CD-MCT) [49, 50]. Analogues to reactive dyes the CD-MCT can be fixed to the fabric by well-known methods and with common equipment. CD-MCT can be applied to fibre surfaces by an exhaustion method or by thermofixation. Moldenhauer with co-workers found out [51] that the fixation was the best when textile substrate was cotton. Mixed fibre materials like cotton/polyurethane or cotton/polyamide can be finished with  $\beta$ -CD-MCT in good yields. Ibrahim et.al [52] reported the improvement of UV protective properties of cotton/wool and viscose/wool blends via incorporating of reactive  $\beta$ -CD-MCT in the easy care finishing formulations, followed by subsequent treatment with copper-acetate or post-dyeing with different classes of dyestuffs (acid, basic, direct and reactive). They found out that post-dyeing of the prefinished textile blends results in a significant increase in the UPF (UV-protection factor) values as a direct consequence of a remarkable reduction in UV radiation transmission through the plain weave fabric.  $\beta$ -CD modified with monochlorotriazine was applied to the cotton fabrics for entrapping of sandalwood oil as an aroma-finishing agent by Sricharussin [53]. The Fourier transform infrared, tensile stress tests and gas chromatography-mass spectroscopy measurements were used to investigate the effects of the treatment. It was found that  $\beta$ -CD-MCT can be fixed to cotton fabrics with the pad-dry-cure method at high temperature. No loss of tensile strength of the treated fabrics was reported. The fragrance disappeared from untreated cotton after 8 days when stored at ambient temperature (30°C) but on other hand, the fragrance was retained in  $\beta$ -CD-MCT-treated cotton fabrics for 21 days in the same conditions. Agrawal et.al compared the efficiency of enzymatic treatments and existing chemical techniques for bonding  $\beta$ -CD and its derivatives to cotton surface. Novel chemical based crosslinking with homo-bi-functional reactive dye (C.I. reactive black 5) and grafting with reactive  $\beta$ -CD-MCT show maximum attachment to cotton surface. Innovative, enzymatic coupling of especially synthesized 6-monodeoxy-6-mono(N-tyrosin-

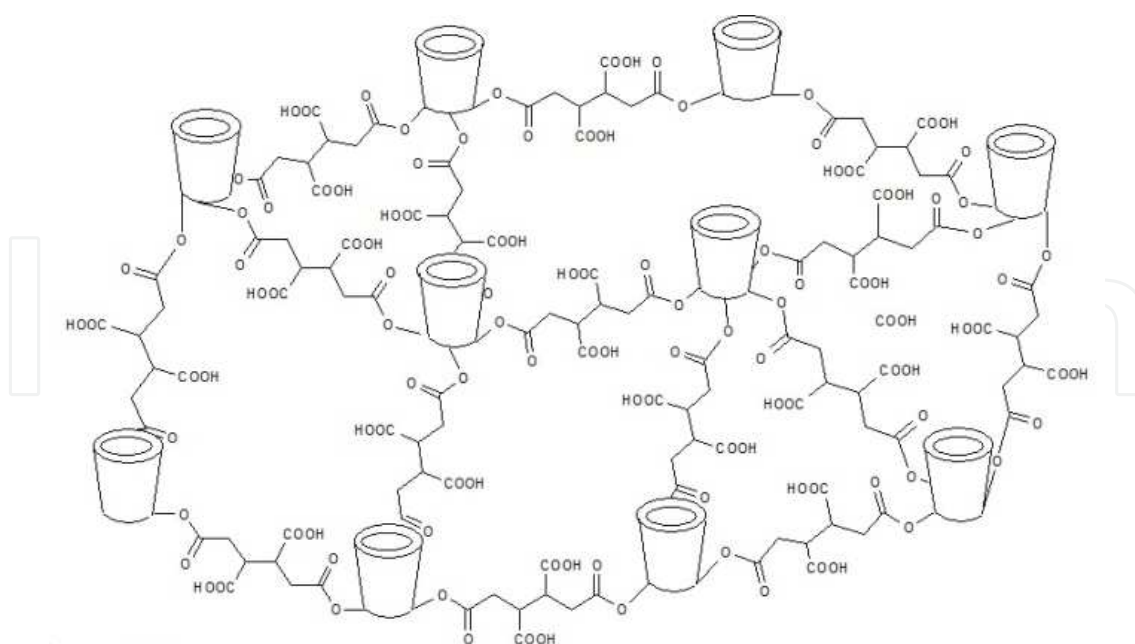


yl)- $\beta$ -cyclodextrin was performed on cotton textile surface at low temperature. Alteration in surface topography has been observed for all  $\beta$ -CD treated samples [54]. Martel with co-workers coupled  $\beta$ -CD-MCT to chitosan, to obtain a chitosan derivative bearing cyclodextrin. Because the average degree of substitution of the CD derivative was 2.8, the reaction yielded crosslinked insoluble products. The structure of these materials has been investigated by high-resolution magic-angle spinning (HRMAS) with gradients. For the first time, HRMAS spectra of chitosan polymers containing  $\beta$ -CD were obtained. This NMR technique produced one- and two-dimensional well-resolved solid-state spectra. Decontamination of waters containing textile dyes were carried out with the crosslinked derivatives. Report by Martel showed that the new chitosan derivatives are characterized by a rate of sorption and a global efficiency superior to that of the parent chitosan polymer and of the well-known cyclodextrin-epichlorohydrin gels [55]. El-Tahlawy with co-workers carried out a novel technique for preparation of cyclodextrin-grafted chitosan.  $\beta$ -CD citrate was synthesized by esterifying of  $\beta$ -CD with citric acid (CA) in presence or absence of sodium hypophosphite as a catalyst in a semidry process.  $\beta$ -CD/grafted chitosan was prepared by coupling  $\beta$ -CD citrate with chitosan dissolved in different formic acid solutions having different concentrations. The reacting ingredients were subjected to various reaction conditions to attain the optimum condition.  $\beta$ -CD/grafted chitosan were evaluated by measuring the nitrogen content of both chitosan and grafted chitosan. Chitosan and  $\beta$ -CD/grafted chitosan, having different molecular weights, were evaluated as antimicrobial agents for different microorganisms [56].

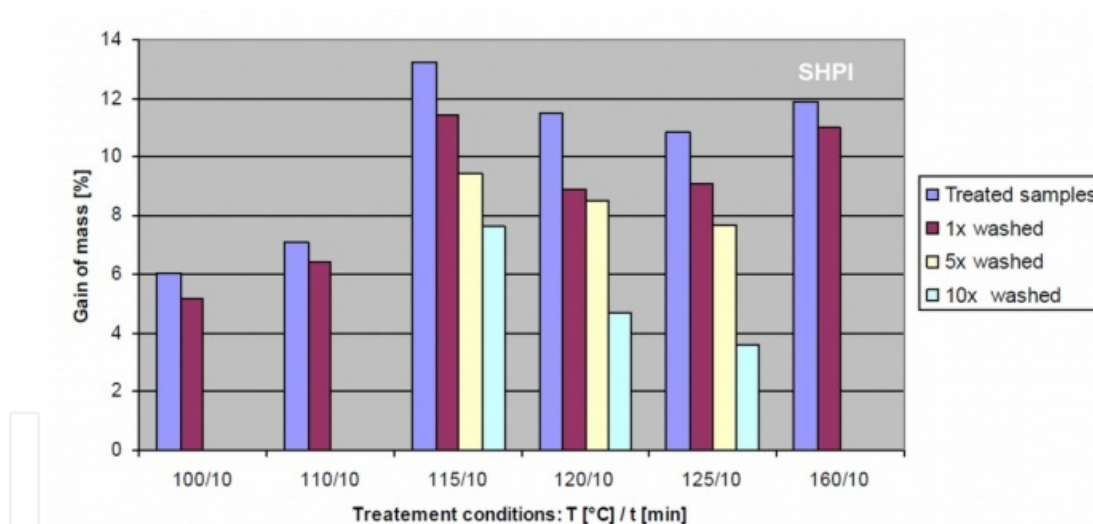
Very effective bonding of CDs on cellulose fibres can be achieved by a high-performance resin finish [57] or with non-formaldehyde reagents such as polycarboxylic acids [58, 59] which can covalently esterify hydroxyl groups of cellulose and CDs and therefore the grafting of CD on cellulose can occur. The same linking/crosslinking reagents can be used in the treatment of different synthetic fibres. Polyester fibres were modified by  $\beta$ -CD using citric acid [7, 59] in research work of our group [60], 1,2,3,4-butane tetracarboxylic acid was used as a linker. Odour control is a very important topic in the apparel and underwear items. Odour can be controlled by applying an antimicrobial finish, removing the odour molecules as they are formed or covering up the odour with a fragrance. The odour molecules being hydrophobic become trapped in the cavities of the CDs and are removed during laundering.

Within our research work PET fibres were treated in aqueous solution of different concentrations of  $\beta$ -CD and BTCA. We reported that BTCA molecules react via anhydride formation with hydroxyl groups of  $\beta$ -CD and form nano-assembly which can be physically attached to the PET fibres surface at the elevated temperature. Such assembly could be schematically presented as shown in Figure 3.

For reducing the termofixation temperature the catalyst cyanamide was used. We concluded that the treatment of PET with  $\beta$ -CD/BTCA was very successful even at temperature as low as 115°C when CA as a catalyst has been used. After 10 washings the gain on mass remained as high as 7.8% (Figure 4).



**Figure 3.** Nano-assembly of  $\beta$ -CD crosslinked with BTCA on textile surface.



**Figure 4.** Samples 100/10, 110/10, 115/10, 120/10 and 125/10 are PET samples treated with  $\beta$ -CD, BTCA, CA at 100, 110, 115, 120 and 125°C, respectively; sample 160/10 was treated with  $\beta$ -CD, BTCA and SHPI at 160°C; all samples were termofixed for 10 minutes.

We were able to reduce the curing temperature to 115°C and prepared nanoencapsulated textile materials with increased adsorption capacity (the adsorption of ammonia gas onto treated and untreated PET textile materials was measured using Japan standard test method - JIS K0804) and with postponed release of volatile compounds. From the ammonia gas adsorption measurements (Table 1), it is possible to conclude that the adsorption of ammonium gas increased when PET fabric was treated with  $\beta$ -CD/BTCA/CA at 115°C/10min - after

one hour of exposure to ammonia gas the concentration of gas in the chamber was zero, compare to the concentration when untreated PET fabric was exposed to the ammonium gas, where the concentration in the chamber was changed from the initial value of 125ppm to 77ppm.

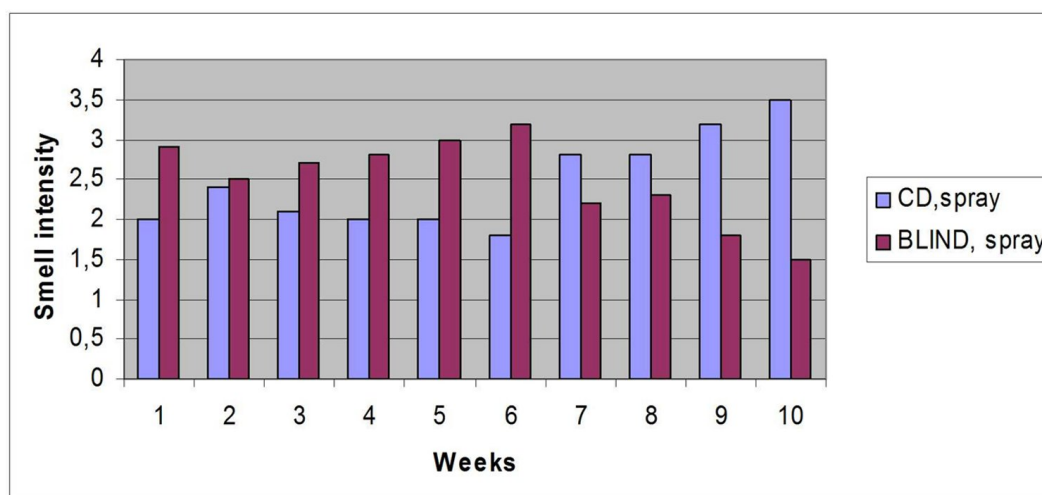
	PET treated with $\beta$ -CD/BTCA/ CA at 115°C/10 min	Untreated PET
Initial concentration (ammonia)	125ppm	125ppm
One hour concentration (ammonia)	0ppm	77ppm

**Table 1.** Decrease of ammonium gas concentration due to the adsorption.

In order to quantify the odour-releasing behaviour of  $\beta$ -CD treated PET fabrics, we organized a sensory panel of nine people to whom the odour was presented under controlled conditions. In order to study the postponed release of the volatile compounds from the  $\beta$ -CD treated textile substrate the following was performed:  $\beta$ -CD/BTCA/CA treated PET textile substrate was sprayed with perfume and dried; the intensity of the perfume from the untreated PET fabric sprayed with perfume was also monitored for comparison purposes. Both treatments were performed in triplets. The size of the clothes was 10 by 10 cm. All with perfume treated textile samples were stored separately in dark places. Samples were stored in open conditions so that the perfume was able to evaporate constantly. The odour release was measured once per week. The smell intensity was evaluated from 0 to 4, where 0 means no smell and 4 means very intensive smell. From Figure 5 it is possible to see that the odour release intensity of untreated PET fabrics sprayed with perfume (BLIND, spray) starts to decrease after 6 weeks; the odour intensity of perfume sprayed on  $\beta$ -CD treated fabrics remains constant, but there is slight indication that the intensity of the perfume starts to increase after 6 weeks. We can conclude that, in the case of  $\beta$ -CD treated PET fabrics, some postponed release of the fragrance occurs.

Glycidyl methacrylate is widely used in the production of polymer coatings and finishes, adhesives, plastics and elastomers, it can be grafted to various textiles substrates as well. Desmet and co-workers functionalized cotton-cellulose by gamma-irradiation-induced grafting of glycidyl methacrylate (GMA) to obtain a hydrophobic cellulose derivative with epoxy groups suitable for further chemical modification. Two grafting techniques were applied. In pre-irradiation grafting (PIG) cellulose was irradiated in air and then immersed in a GMA monomer solution, whereas in simultaneous grafting (SG) cellulose was irradiated in an inert atmosphere in the presence of the monomer. In the paper authors claimed that the PIG led to a more homogeneous fibre surface, while SG resulted in higher grafting yield but showed clear indications of some GMA-homopolymerization. Effects of the reaction parameters (grafting method, absorbed dose, monomer concentration, solvent composition) were evaluated by SEM, gravimetry (grafting yield) and FT-IR spectroscopy. It is reported that water uptake of the cellulose decreased while adsorption of pesticide molecules increased upon grafting. The adsorption was further enhanced by  $\beta$ -CD immobilization during SG.

This method can be applied to produce adsorbents from cellulose based agricultural wastes [61]. CDs can be incorporated into fibres during the spinning processes [62, 63].



**Figure 5.** Odour intensity of PET fabrics pre-treated with  $\beta$ -CD (blue) and untreated PET fabrics sprayed with the perfume.

Electrospinning is proven to be an effective method for producing non-woven mats of fibres with high aspect ratios. Manasco and co-workers reported the preparation of submicron hydroxypropyl-beta-cyclodextrin (HP- $\beta$ -CD) fibres by electrospinning without the addition of a carrier polymer. They focused on exploring solution properties that make fibre formation possible contrary to the widely accepted premise that molecular entanglement of macromolecules is required for electrospinning. The ability to electrospin from these solutions was attributed to hydrogen-bonded aggregation between HP- $\beta$ -CD molecules at high concentrations [64]. Further it is reported by Uyar and co-workers that poly(methyl methacrylate) (PMMA) nanofibres containing the inclusion complex forming  $\beta$ -CD were successfully produced by means of electrospinning in order to develop functional nanofibrous webs. Electrospinning of uniform PMMA nanofibres containing different loadings of  $\beta$ -CD (10%, 25% and 50% (w/w)) was achieved. The surface sensitive spectroscopic techniques; X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) showed that some of the  $\beta$ -CD molecules are present on the surface of the PMMA nanofibres, which is essential for the trapping of organic vapours by inclusion complexation. Direct pyrolysis mass spectrometry (DP-MS) studies showed that PMMA nanowebs containing  $\beta$ -CD can entrap organic vapours such as aniline, styrene and toluene from the surroundings due to inclusion complexation with beta-CD that is present on the fibre surface. The study showed that electrospun nanowebs functionalized with CDs may have the potential to be used as molecular filters and/or nanofilters for the treatment of organic vapour waste and air filtration purposes [65]. Polyvinyl alcohol (PVA) nanowebs incorporating vanillin/cyclodextrin inclusion complex (vanillin/CD-IC) were produced via electrospinning technique by Kayaci and Uyar [66]. The vanillin/CD-IC was prepared with three types of CDs;  $\alpha$ -CD,  $\beta$ -CD and  $\gamma$ -CD to find out the most favourable CD type for the stabili-

zation of vanillin. PVA/vanillin/CD-IC nanofibres, having fibre diameters similar to 200 nm, were electrospun from aqueous mixture of PVA and vanillin/CD-IC. The results indicated that vanillin with enhanced durability and high temperature stability was achieved for PVA/vanillin/CD-IC nanowebs due to complexation of vanillin with CD. Additionally, they reported that PVA/vanillin/ $\gamma$ -CD-IC nanoweb was more effective for the stabilization and slow release of vanillin suggesting that the strength of interaction between vanillin and the  $\gamma$ -CD cavity is stronger when compared to  $\alpha$ -CD and  $\beta$ -CD.

### 3.1.2. *Cosmetotextiles*

Although still in its infancy, the market for cosmetotextiles - often referred to as "wearable skincare" - is set to grow rapidly, and the textile industry is optimistic that further technical developments will open up new markets and create growing business opportunities [67]. Cosmetotextile became a fast growing new branch of specialized micro- or nano-encapsulation textile products, with most patents issued after the 1990 [68]. The physical and chemical properties of the guest molecules encapsulated in CDs can change due to complex formation. Thus, for example, the stability of the complexed molecule against light and oxygen increases and the vapour pressure is reduced. The solubility of slightly soluble molecules increases in a CD complex. All these and further advantages of CDs and their complexes can be used for the formulation of cosmetic products [69]. Cosmetotextile allows the administration of active molecules simply and controllably. It can also be used to change the surface properties of a fabric in order to make it self-cleaning, hydrophobic or lipophobic. The article prepared by Ripoll and co-workers reviews the current state of the art concerning functionalization techniques and the methods used to characterize various functionalized fabric. This review also reveals the surprising lack of publications on the functionalization of textile supports [70].

Moist oils (essential oils, herbal oils, oils from flower seeds) have skin care benefits in that they provide an occlusive layer that lubricates the epidermis, together with a moisturizing effect that helps to prevent excess water loss. Essential oils attributed with a range of properties that help to achieve physical and emotional balance. Besides, one additional advantage of molecular encapsulation is the possibility to reload them 4, 58, 71. Cosmetotextile applications can be used in the treatment of chronic venous insufficiency in legs by means of elastic bandages loaded with natural products which possess flebotonic properties. Cravotto and co-workers 72 have developed an efficient synthetic procedure for the preparation of  $\beta$ -CD-grafted viscose by means of the 2-step ultrasound-assisted reaction. The highly grafted fabric bearing bis-urethane bridged  $\beta$ -CD has been characterized by ATR FT-IR and CP-MAS spectra and by an empiric colorimetric method which used phenolphthalein as the CD guest. They have also developed a suitable cosmetic preparation containing natural substances and extracts (aescin, menthol, Centella asiatica and Ginkgo biloba) to recharge the CD-grafted textile. The efficacy of the new cosmetotextile has been corroborated by in vitro studies of diffusion through membranes, cutaneous permeation and accumulation in porcine skin. Aescin was taken as a reference compound and its concentration in the different



compartments was monitored by HPLC analysis. They reported that this cost effective cosmetotextile showed excellent application compliance and was easily recharged.

Electrospun functional polystyrene (PS) fibres containing CD-menthol inclusion complexes are new and advance class of cosmetotextiles. Uyar and co-workers developed functional electrospun fibres containing fragrances/flavours with enhanced durability and stability assisted by CD inclusion complexation. As a model fragrance/flavour molecule they used menthol. CD-menthol inclusion complexes were incorporated in electrospun PS fibres by using three types of CDs:  $\alpha$ -CD,  $\beta$ -CD and  $\gamma$ -CD. It is reported that due to complexation of menthol with CDs, the stabilization of menthol was achieved up to 350°C whereas the PS fibres without the CD complex could not preserve volatile menthol molecules. This study suggested that the electrospun fibres functionalized with CD are very effective for enhancing the temperature stability of volatile fragrances/flavours and therefore show potentials for the development of functional fibrous materials [73].

Today the subject of well-being is an area which is receiving much interest, with scent being one of the most important aspects of personal care. The definition of the word aromatherapy is the following: therapeutic uses of fragrances which at least mere volatilize to cure and to mitigate or cure diseases, infection and indisposition by means of inhalation alone [74]. The term aromachology was coined in 1982 to denote the science that is dedicated to the study of the relationship between psychology and fragrance technology to elicit a variety of specific feelings and emotions – such as relaxation, exhilaration, sensuality, happiness and well-being-through odours.

CDs linked on cellulose do not affect the cellulose's properties, and CDs keep their ability to form inclusion complexes with other suitable molecules thus, CDs are the first choice in preparing aromatherapy textiles. Lavender is the most used and most versatile of all the essential oils. It is very useful oil, especially when symptoms are due to a nervous problem. The effects of lemon, camomile, rose, cardamom, clove, and jasmine fragrance oils on human have been confirmed by many research works. The sedative effects for the pharmaceutical and emotional effects of essential oils are listed in Tables 2 and 3 respectively [75, 76].

### *3.1.3. Miscellaneous applications of cyclodextrins in textile industry*

An insect repellent is a substance applied to skin, clothing, or other surfaces which discourages insects from landing or climbing on that surface. Synthetic repellents (such as paradichlorobenzene) tend to be more effective than 'natural' repellents, but on the other hand they are usually toxic. Cedar oil is often used as a natural insect repellent or it is used for its aromatic properties, especially in aromatherapy. Essential oil repellents tend to be short-lived in their effectiveness due to their volatile nature. To prevent the essential oils from evaporating from the textile materials we can encapsulate them in  $\beta$ -CD. In our research group [80, 81] with  $\beta$ -CD, nanoencapsulated wool and PET/wool blend fibres were further treated with cedar oil, which is known for being a natural insect repellent. The complex formation of cedar oil with  $\beta$ -CD was determined by ATR FT-IR spectroscopy. Textile material containing  $\beta$ -CD showed, after being treated with cedar oil, a prolonged moths oppression compared to those textile materials treated only with cedar oil. Table 4 presents the damages to wool and larval conditions according to the time of

exposure. No visible damage was observed to the naked eye when  $\beta$ -CD/cedar oil treated wool was exposed to a moth’s colony for 2 months. In the control (wool samples treated only with cedar oil) no damage was observed for the first few days, but when the cedar oil had evaporated, the wool cloth was not protected anymore. In contrast, when the cedar oil was encapsulated in the  $\beta$ -CD cavity, evaporation was hindered and resistance to insect pests’ activities regarding cedar oil remained.

Effects	Essential Oil
Sedation	Mint, Onion, Lemon, Metasequoia
Coalescence	Pine, Clove, Lavender, Onion, Thyme
Diuresis	Pine, Lavender Onion. Thyme, Fennel, Lemon, Metasequoia
Facilitating Menses	Pine, Lavender. Mint, Rosemary, Thyme, Basil, Chamomile, Cinnamon, Lemon
Dismissing sputum	Onion, Citrus, Thyme, Chamomile
Allaying a fever	Ginger, Fennel, Chamomile, Lemon
Hypnogenesis	Lavender, Oregano, Basil, Chamomile
Curing Hypertension	Lavender, Fennel, Lemon, Ylangylang
Be good for stomach	Pine, Ginger, Clove, Mint, Onion, Citrus, Rosemary, Thyme, Fennel, Basil, Cinnamon
Diaphoresis	Pine, Lavender, Rosemary, Thyme, Chamomile, Metasequoia
Expelling wind	Ginger, Clove, Onion, Citrus, Rosemary, Fennel, Lemon
Losing weigh	Onion, Cinnamon, Lemon
Relieving pain	Vanilla, Lavender. Mint, Onion, Citrus, Rosemary, Chamomile, Cinnamon, Lemon
Detoxification	Lavender
Curing diabetes	Vanilla, Onion, Chamomile, Lemon
Stopping diarrhea	Vanilla, Ginger, Clove, Lavender, Mint, Onion, Oregano, Rosemary, Thyme, Chamomile, Cinnamon, Lemon
Curing flu	Pine, Lavender, Mint, Onion, Citrus, Rosemary, Thyme, Chamomile, Cinnamon, Metasequoia
Curing rheumatism	Lavender, Onion, Citrus, Rosemary, Thyme, Metasequoia
Urging sexual passion	Pine, Ginger, Clove, Mint, Onion, Rosemary, Thyme, Fennel
Relieving spasm	Cinnamon
Promoting appetite	Clove, Lavender, Mint, Onion, Citrus, Rosemary, Fennel, Basil, Chamomile, Cinnamon, Lemon, Metasequoia
Relieving cough	Rosemary

**Table 2.** Pharmaceutical effect of essential oils [75, 77, 78].

Emotion	Essential Oils with the Sedative Effects
Anxiety	Benzoin, Lemon, Chamomile, Rose, Cardamom, Clove, Jasmine
Lament	Rose
Stimulation	Camphor, Balm oil
Anger	Chamomile, Balm oil, Rose, Ylangylang
Wretchedness	Basil, Cypress, Mint, Patchouli
Allergy	Chamomile, Jasmine, Balm oil
Distrustfulness	Lavender
Tension	Camphor, Cypress, Vanilla, Jasmine, Balm oil, Lavender, Sandalwood
Melancholy	Basil, Lemon, Chamomile, Vanilla, Jasmine, Lavender, Mint, Rose
Hysteria	Chamomile, Balm oil, Lavender, Jasmine
Mania	Basil, Jasmine, Pine
Irritability	Chamomile, Camphor, Cypress, Lavender
Desolation	Jasmine, Pine, Patchouli, Rosemary

**Table 3.** The sedative or emotion effects of essential oils [75, 79].

Time	$\beta$ -CD/cedar oil treated wool	Cedar oil treated wool	Untreated wool
48h	No detectable damage	No detectable damage	Very slight visible damage
	Larval conditions: live	Larval conditions: live	Larval conditions: live
72h	No detectable damage	No detectable damage	Moderate visible damage
	Larval conditions: dead	Larval conditions: dead	Larval conditions: live
7 days	Addition of new larvae	Addition of new larvae	/
14 days	No detectable damage	Very slight visible damage	Very heavy damages
	Larval conditions: dead	Larval conditions: live	Larval conditions: live
56 days	No detectable damage	Moderate visible damages	Very heavy damages
	Larval conditions: dead	Larval conditions: live	Larval conditions: live, pupating

**Table 4.** The estimation of wool damage and the condition of larval colony in accordance to elapsed time.

To maintain antimicrobial activity, frequent administration of conventional formulations of many antibiotics with short half-life is necessary. To enhance release properties, many materials have been introduced into the matrix and coating extended-release system in the past few years. The review by Gao [82] highlights the development of materials used in extended-release formulation and nanoparticles for antibiotic delivery. CDs are mentioned as nanoparticles/nanocarriers which allow the antibiotic extended-release.

A textile polyester vascular graft can be modified by methyl- $\beta$ -CD to obtain a new implant capable of releasing antibiotics directly in situ at the site of operation over a prolonged period and thereby preventing post-operative infections [83]. Wang reported the inclusion complex of miconazole nitrate with  $\beta$ -CD formation by the co-precipitation method. The DSC curve and X-ray diffraction verified the inclusion complex formation between  $\beta$ -CD and miconazole nitrate. The skin-care textiles can be obtained by treating fabrics with inclusion complexes using the sol-gel method [84].

Novel nano-porous polymers or nanosponges can be prepared for removal of organic pollutants from waste water. The polymeric «nanosponge» materials are not durable (usually they are in gel form), they do not have high mechanical strength, so they must be impregnated onto the pore structure of a ceramic or some other porous surfaces [85, 86]. This technology is very specific for the target pollutant, it is very expensive and the removal of the adsorbed pollutant from the nanosponge is not possible. Textile materials are very important as filter materials. The cost of textile materials is acceptable (polyester, viscose), they have sufficient mechanical strength; the pore size, especially the macro-pore size can vary and it depends on the type of textile (the density of non-woven material) and on the diameter of the fibres. Textile materials can be further modified to prepare filtration materials with additional adsorption.

The amount of aromatic organic pollutants (phenols, aniline, formaldehyde and others) can be reduced from dyeing wastewater by using CDs which can be immobilized on a water insoluble organic support. The new concept for modification of textile substrates based on permanent fixation of supramolecular compounds - CDs on the material surface thus imparts new functionality to the fabric [87]. The guest molecules could be various organic molecules and some metal ions as well. The assembly of nanocapsules on textile materials acts as selective filtration/adsorption media for various pollutants. Prabhakaran and Mano further reported that CDs have recently been recognized as useful adsorbent matrices. Due to its hydrophobic cavity, CDs can interact with appropriately sized molecules to result in the formation of inclusion complexes. These complexes are of interest for scientific research as they exist in aqueous solution and can be used to study the hydrophobic interactions which are important in the biomedical and environmental fields. The grafting of CD onto chitosan can result in the formation of a molecular carrier that possess the cumulative effects of inclusion, size specificity and transport properties of CDs as well as the controlled release ability of the polymeric matrix. In this review, different methods of CD grafting onto chitosan are discussed [88]. Electrospinning has been used to create polystyrene (PS) nanofibres containing any of the three different types of cyclodextrin (CD);  $\alpha$ -CD,  $\beta$ -CD, and  $\gamma$ -CD [89]. These three CDs are chosen because they have different sized cavities that potentially allow for selective inclusion complex (IC) formation with molecules of different sizes or differences in affinity of IC formation with one type of molecule. The comparative efficiency of the PS/CD nanofibres/nanoweb for removing phenolphthalein, a model organic compound, from solution was determined by UV-Vis spectrometry, and the kinetics of phenolphthalein capture was shown to follow the trend PS/ $\alpha$ -CD > PS/ $\beta$ -CD > PS/ $\gamma$ -CD. Direct pyrolysis

mass spectrometry (DP-MS) was also performed to ascertain the relative binding strengths of the phenolphthalein for the CD cavities, and the results showed the trend in the interaction strength was  $\beta$ -CD >  $\gamma$ -CD >  $\alpha$ -CD. Results of their research demonstrated that nanofibres produced by electrospinning that incorporate CDs with different sized cavities can indeed filter organic molecules and can potentially be used for filtration, purification, and/or separation processes.

## 4. Conclusion

Since 1980, when Szejtli first patented the bonding of CDs onto textile fibres, a lot of research has gone into the application of CDs on to textile substrates. But there is still a gap between original high level basic science and commercial applications of CDs in all industrial sectors.

Nevertheless the use of CDs in the textile industry has increased in the last years. Grafted CDs on textile substrates or spun fibres which contain CDs can be used to obtain special functionality of textiles such as absorption; they can complex and release fragrances or “skin-care-active” substances like vitamins, caffeine and menthol as well as bioactive substances such as biocides and insecticides and drugs. Furthermore, various textile materials treated with CDs could be used for adsorption of small pollutants from waste waters - for filtration, purification, and/or separation treatments of waste waters.

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