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## Application of cyclodextrins in textiles

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#### Abstract

Cyclodextrins are cyclic oligosaccharides obtained by enzymatic degradation of starch. The macrocyclic cyclodextrins were discovered in 1891, and the structures were elucidated in the mid-1930s. Their industrial significance become obvious in the 1970s, now thousands of tons of the three cyclodextrins ( $\alpha$ ,  $\beta$ -, and  $\gamma$ -CD) and of their chemical derivatives and inclusion complexes are produced industrially. The outer surface of these doughnut-shaped molecules is hydrophilic, but they possess an axial open cavity, which is of hydrophobic character and capable of including other apolar molecules in case of geometric compatibility. This is the essence of molecular encapsulation by inclusion complex formation. In the last few years, the new direction in textile research is the functionalisation of textile systems. It is believed that  $\beta$  -cyclodextrin play a very important role in these new developments.  $\beta$  -cyclodextrin can act as a host for various guest molecules. This enables the development of fabrics that release chemical compounds such as fragrances and antimicrobial agents, waste water treatment. It is believed that there are many possibilities for the development of new textile products with advanced properties based on  $\beta$  -cyclodextrin.

Keywords: cyclodextrin, oligosaccharides, enzymatic degradation, hydrophilic, antimicrobial agents

#### Introduction

Since the first reference to cyclodextrin in a publication in 1891 and its first patent in 1953, cyclodextrin has been of great interest to researchers <sup>[6]</sup>. Since 2009, the total number of cyclodextrin related publications amounts to 42,000, with a daily average of 7 publications in 2009, giving an indication of its wide applicability and research interest. The application of cyclodextrins in textiles is really not new. However, there is still room for development of new products with advanced properties based on cyclodextrins. Cyclodextrins are cyclic oligosaccharides composed of glucose units linked by a-1, 4-glycosidic bonds. There are three types;  $\alpha$ -cyclodextrin,  $\Box$ -cyclodextrin,  $\gamma$ -cyclodextrin, which are composed of 6, 7, and 8 a-1, 4-glycosidic bonds as shown in Figure. Each cyclodextrin unit has a hydrophobic cavity which can act as a host for a hydrophobic guest molecule. This property comes in useful for solubilising and stabilising highly hydrophobic molecules in solvents such as water. No hydrogen bonds are formed or broken during the formation of such host-guest complexes. Solubilising is also said to occur through the formation of micellar types of aggregate in aqueous solutions. The combination of  $\Box$ -CD and textiles to create new functionalised fabrics therefore received a lot of attention over the last decade <sup>[6]</sup>.

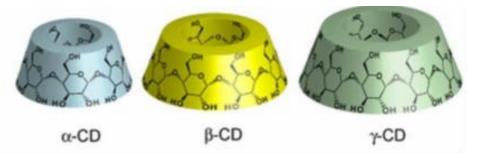


Fig 1: Structure of  $\alpha$  -cyclodextrin,  $\beta$  -cyclodextrin,  $\gamma$  -cyclodextrin <sup>[8]</sup>

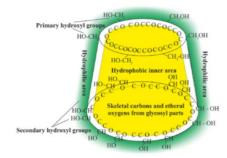


Fig 2: Basic principle of Alpha-CD conformation [5].

Research work mainly pertaining to  $\Box$ -CD fixation to textiles and their application in functionalised textiles are covered in this review paper. This paper offers a wide overview of applications of  $\Box$ -CD in textiles, and this is of special interest to textile researchers working on adding functionality to textile surfaces. The role of  $\Box$ -CD as a treating and sizing agent has not been dealt with in this paper.  $\Box$ -CD is the most interesting of the cyclodextrins available due to its ease of production, price, ease of attachment to textile surfaces and the size of the cavity which makes it suitable for hosting a range of guest molecules. The paper also deals with certain finer aspects, such as characterisation methods, applications, and incorporation techniques of  $\Box$ -CDs on textiles [6].

#### **Properties of Cyclodextrins**

The most notable feature of CDs is their ability to form solid inclusion 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 [7]. No covalent bonds are broken or formed during formation of the inclusion complex. According to some authors 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 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 [7].

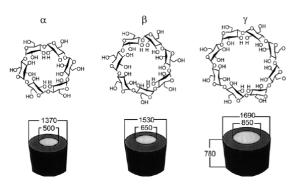


Fig 3: Chemical structures of cyclodextrins <sup>[1]</sup>

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 [7]. 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. 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 stoic metric 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 [7].

These properties are:

- Solubility enhancement of highly insoluble guests,
- Stabilisation of labile guests against the degradative effects of oxidation,
- 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.

#### Physicochemical properties of α-, β- and γ-cyclodextrin 1. Polarity of cyclodextrins

As a result of the frusto-conical structure and the particular position of the hydroxyl, cyclodextrins are amphiphilic and thus have two distinct zones of polarity. The exterior of the cavity and the pole ends are: This is essentially due to the hydroxyl and thus promotes the solubilization in very polar solvents. In contrast, the interior of the cavity where the only oxygen's interglucosiques is polar months and this area is more hydrophobic <sup>[4]</sup>.

#### 2. Stability and solubility of cyclodextrins

Several factors such as temperature, solvent and pH were influenced stability cyclodextrins. They are stable in an

alkaline medium but may undergo partial acid hydrolysis at a pH below 3.5 and at a temperature higher than 60 °C, producing glucose, and a series of acyclic maltosaccharides. Coleman *et al.* were attributed the low solubility of  $\beta$ -CD having a symmetry axis 7, with the  $\beta$ -CD aggregation there between due to unfavourable interactions of hydrogen bonds with water. Szejtli proposes that the intramolecular hydrogen bonds of hydroxyl  $\beta$ -CD (more rigid) are responsible for its low solubility. The  $\alpha$ -CD and  $\gamma$ -CD more flexible and having one, two or three glucose units inclined, do not contain this continuous belt of hydrogen bonds secondary hydroxyl (O2 and O3). And therefore, favour the hydrogen bonds with the solvent, thereby increasing their aqueous solubility. Alkylation of the hydroxyl of the  $\beta$ -CD significantly increases the solubility, and this phenomenon, a priori surprising, the subject of substantial research. Eventually the cyclodextrins are soluble in water and polar aprotic solvents such as DMSO, DMF and pyridine [4].

Table 1: Physicochemical	properties of	the main nativ	e CDs [4].

Properties	α-CD	β-CD	γ-CD
Number of glucose units	6	7	8
Empirical formula (anhydrous)	C36H60O30	C42H70O35	C48H80O40
Atomic mass (anhydrous) g / mol	972,85	1134,99	1297,14
Cavity length (Å)	7,9-8	7,9-8	7,9-8
Cavity diameter (Å)	4,7-5,3	6,0-6,6	7,5-8,4
Outside diameter (Å)	14,6-15	15,4-15,8	17,5-17,9
Volume of the cavity (Å3)	174	262	427
pKa at 25 ° C	12,332	12,202	12,081
Melting point (°C)	275	280	275
Optical rotation $\alpha D$ at 25 °C (°)	149,5- 150,5	162-163	176,9- 177,9
Solubility (eau,25°C),mol/L	0,1211	0,0163	0,168
Solubility (eau,25°C), g/100 ml	14,5	1,85	23,2
Hydration CD,nH2O	n = 6 to 7	n = 10 to $12$	n = 7 to 13

## General industrial applications of β -CDCosmetics, personal care and toiletry

In this sector, cyclodextrins involved in the stabilization, odour control and process improvements in the conversion of a liquid component in a solid form. The applications of cyclodextrins in this area include toothpaste, skin creams, liquid and solid fabric softeners, paper towels, tissues and underarm shields. In fact, the interaction of the guest with CDs produces a higher energy barrier to prevent volatilization, producing lasting fragrance [4].

### 2. Cyclodextrins in pharmaceutical industry

Cyclodextrins complexation uses are well known in the pharmaceutical industries that have been certified by several critics in recent years. Thanks to their non-toxicities, the use of CDs is very important in the bioavailability, the active stabilization, odour or taste masking, reducing irritation and uses handling equipment. Then the practical use of natural cyclodextrins as drug carriers is restricted to their low aqueous solubility. Table 2 lists cyclodextrin based commercially available pharmaceutical products [4].

## 3. Cyclodextrins in agricultural and chemical industries

A wide variety of agricultural chemicals with cyclodextrins form complexes, including herbicides, insecticides,

fungicides, repellents, pheromones and growth regulators. Indeed, in the grain treated with certain amylases which degrade starch blocks seeds are inhibited. Initially, the plant grows more slowly, but later on this is largely compensated by an improvement of the growth plants producing a crop of 20 to 45% greater 28. There after recent developments imply cyclodextrin glucotransferases (CGTases) in 28, plants. While in the chemical industry, cyclodextrins are widely used to separate the isomers and enantiomers, for catalysing reactions to help various processes and to remove or detoxify waste. Also, cyclodextrins are widely used in the separation of enantiomers by high performance liquid chromatography (HPLC) or gas chromatography (GC). There are other analytical applications can be found in the spectroscopic analysis. But for nuclear magnetic resonance studies (NMR), the CDs may act as chiral shift agents and in that the circular Dichroism (chiral) selective modifying agents' spectra. Cyclodextrins may be used in electrochemistry to mask contaminant compounds, which allows for more precise determinations [4].

## 4. Cyclodextrins in environmental

In the environmental field cyclodextrins play a very important role in terms of solubilization of organic contaminants, enrichment and the removal of organic pollutants and heavy metals from the soil, water and Atmosphere. CDs have been used in water treatment to increase stabilization of the action, encapsulation and adsorption of contaminants. In 1999, Reid *et al.* discussed the soil test to determine the bioavailability of pollutants using CD and its derivatives. Cyclodextrins makes three benzimidazole fungicides (thiabendazole, carbendazim and fuberidazole) more soluble in water which causes the availability of its fungicides to soil. More CDs have the ability to increase the solubility of the hydrocarbon for the biodegradation, bioremediation and also reduce the toxicity resulting in increased microbial and plant growth. Thus 90% of the toxic material is disappear [4].

## 5. Cyclodextrins in food technology

Cyclodextrins have found numerous applications in the food industry. They form inclusion complexes with a variety of molecules including fats, flavours and colorants. Also, they are used to remove and hide the unwanted components and to salt out the desired components with time. Cyclodextrins are also used to protect and relegate aromas. Natural and artificial flavours or oils are volatile liquids and complexation with cyclodextrins provides a promising alternative to conventional encapsulation technologies for the protection of aromas. For example, complexation of sweeteners such as aspartame with cyclodextrin stabilizes and improves its taste. It also eliminates the bitter taste of other sweeteners such as stevioside and rubusoside. Flavonoids and terpenoids are good for health because of their antioxidant and antimicrobial properties but cannot be used as food because of their low solubility and bitter taste. Sumiyoshi discussed improving the properties of these compounds by complexing with cyclodextrin [4].

## 6. Cyclodextrins in catalysis

Cyclodextrins and their derivatives are used in the field of catalytic chemistry. For example, Atwood explained the use of  $\alpha$ -cyclodextrin in the modified porphyrin reduction of Mn (III). Ye *et al.* found that the use of a derivative of  $\beta$ -cyclodextrin as a catalyst increases the benzyl alcohol conversion rate to aldehyde. Because of their steric effects,

cyclodextrins plays a significant role in the biocatalytic process by increasing the enantioselectivity. Leventis and Silvius have shown that the cholesterol cyclodextrins accelerate the transfer rate between the lipid vesicles [4].

### 7. Cyclodextrins in analysis

In chromatography, cyclodextrins are used extensively in the separation of chiral molecules for their ability to distinguish between the position isomers, groups' fontionnels, homologues and enantiomers. This property is in fact one of the most useful agents for a range of separations. They are still used as ligands chemically bonded or absorbed in the stationary phase or the mobile phase. Currently, chiral separations are one of the most important areas of application of cyclodextrins and their derivatives [4].

#### 8. Cyclodextrins in polymers, adhesives and coatings

Cyclodextrins are used as additives and blowing agents compatible with hot melt systems. They also increase the stiffness, adhesion of hot melt adhesives and interaction between the associative thickener polymer molecules in emulsion-type coatings such as paints tends to increase viscosity. So, in the literature, CDS can be used to counteract this adverse effect [4].

## 9. 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 Nano sponges" [4].

## β -CD and Textiles

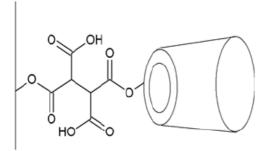
 $\Box$ -CD can be incorporated onto textile by means of spraying, printing, padding, grafting, surface coating, impregnation, ink jet printing or via sol gel, etc. Table shows the various feasible interactions between  $\Box$ -CD and some textile fibres <sup>[6]</sup>.

Parameter	Cotton	Wool	Polyester	Polyamide	Polyacrylonitrile	Polypropylene
Ionic interactions	Not possible	possible	Not possible	Possible	possible	Not possible
Covalent bonds	possible	possible	Not possible	Possible	Not possible	Not possible
Van der Waal forces	Not possible	Not possible	possible	possible	possible	Not possible
Crosslinking agents	possible	possible	Possible	Not possible	Not possible	Not possible
Graft polymerisation	possible	possible	possible	possible	possible	possible

**Table 2:** Feasible interactions between  $\Box$ -CD and some textile fibres <sup>[6]</sup>.

#### Fixation of $\beta$ -CD onto textiles

Listed in the literature among various mechanisms to fix  $\beta$  - CD to fibres, a large volume of them are on grafting with the use of crosslinking agents such as polycarboxylic acids onto cotton, wool, polyester, polyamide and polyacrylonitrile fibres, etc among others. The crosslinking mechanism of crosslinking agents, such as 1,2,3,4, butanetetracarboxylic acid (BTCA) as shown in Figure, is through the formation of a five-member anhydride intermediate. This reacts with the hydroxyl groups of cellulose and/or  $\beta$  - CD through esterification, as shown in Figure. Therefore, citric acid acts as a crosslinking agent providing cotton with anti-wrinkle properties, and it also connects  $\beta$  -CD to cotton <sup>[6]</sup>.



**Fig 4:** Grafting of □-CD via 1,2,3,4, butanetetracarboxylic acid (BTCA) onto a cotton textile

Resins such as epicholorohydrin can also be used to fix  $\beta$ -CD to cellulose. The use of butyl acrylate for the grafting of the monochlorotriazinyl derivative of b-CD (MCT- $\beta$ -CD, shown in Figure) to cellulose fibres is mentioned, and in another case the grafting of glycidal methacrylate of  $\beta$ -CD or MCT- $\beta$ -CD to polyamide fibres or the same to  $\beta$ -CD and polypropylene is discussed.

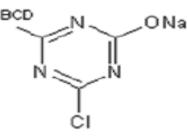


Fig 5: Structure of monochlorotriazinyl functional group of MCT-CD molecule.

MCT-  $\beta$  -CD can be used to permanently bind  $\beta$ -CD to cotton with the conventional reactive dyeing method. The reactive chlorine atom of triazinyl groups of MCT- β -CD can react with nucleophilic residues such as -NHR, -OH, -SH, etc. to form covalent bonds, as shown in Figure. Different substituents for  $\beta$  CDs with absorptive properties can be obtained from MCT-  $\beta$ -CD, which can be attached through electrostatic or hydrophobic interactions. β-CDs can be covalently connected via heterobifunctional reactive dyes which contain monochlorotriazine and vinyl sulphone groups. Non-ionic  $\beta$ -CD derivatives can be fixed to hydrophobic textiles (such as polyamide, polyester and polyacrylonitrile) via the disperse dyeing method through hydrophobic interactions, and cationic  $\beta$ -CD derivatives can be fixed to, for instance, polyacrylonitrile under basic dyeing conditions. B-CD and their derivatives can also be added to a synthetic pellet melt mixture in addition to being electrospun into nanofibers with polymers such as poly methyl methacrylate. Fixing of  $\beta$ -CD via the sol gel process has also been done with the use of tetraethoxysilane and 3-Glycidyloxypropyltrimethoxysilane.

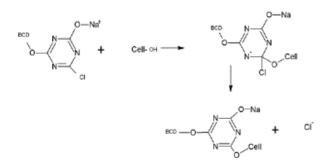


Fig 6: Attachment of MCT-□-CD to cotton.

### Newer fixation methods

In addition, newer methods of fixing  $\beta$ -CDs include the use of homobifunctional reactive dyes such as Reactive Black 5. The attachment of  $\beta$ -CD with homobifunctional reactive dyes can be done in a one step process with the  $\beta$ -CD added to the dye bath during the dyeing. Due to the presence of two reactive groups in the dye there is an increased possibility of the attachment of  $\beta$ -CD and to the cotton surface compared to that of a heterobifunctional reactive dye.

Another new method of attachment is  $\beta$ -CD derivative attached to the tyrosyl group (Tyr- $\beta$ -CD), which can be fixed onto an aminised cotton surface with aromatic amines on its surface. This derivative is named 6-monodeoxy-6-mono (N-tyrosinyl)- $\beta$ -cyclodextrin through the IUPAC nomenclature <sup>[6]</sup>.

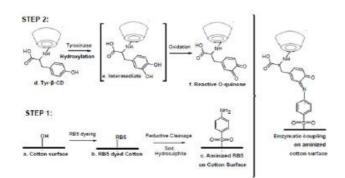


Fig 7: Schema of attachment of Tyr-□-CD to a functionalised cotton textile.

The aminisation of the fabric can be achieved by previously dyeing the textile with a reactive dye with an amine group, and then reducing the dye it to produce free aromatic amines on the textile surface. Such an aminised fabric can be attached to the quinone groups of the tyrosinase enzyme mediated Tyr- $\beta$ -CD, as shown in Figure. Agrawal *et al.* note that fixation with homobifunctional dye and with Tyr- $\beta$ -CD result in higher amounts of  $\beta$ -CD on the fabric compared to any other method, including attachment of tyrosinase mediated Tyr- $\beta$ -CD to a non-reduced reactive dyed fabric.

## End applications of $\beta$ -CD in the textile industry Textile processing

There is a vast amount of literature on the influence of  $\beta$ -CDs on dyeing. It has been reported that  $\beta$ -CDs can absorb dyes and can therefore be used to reduce loss of dye in waste water, in addition to improved dye uniformity and preventing the running of dyes during washing. For instance, dyeing of cotton-polyester blends with disperse dyes and  $\beta$ -CDs led to an improved dye strength and deeper dye shades. Disperse dyeing of cellulose acetate treated with  $\beta$ -CD showed

similarly improved colour intensity as well as the possibility of dyeing at lower temperatures than conventionally used. β-CD can also act as retardant with dyes with which it can form complexes. β-CD can replace the role of surfactants used in dyeing without the loss of dyeing quality, and also improve washing fastness in the case of nylon and cotton with reactive-disperse dyes. Dyeing and easy-care finish can be achieved by using a formulation containing a reactive dye, MCT- $\beta$ -CD and a resin <sup>[6]</sup>. DMDHEU is a crease resistance finish compound used to give wrinkle resistance to textile fabrics. This finish however, leads to a loss of formaldehyde during use. Researchers treated fabrics with the crease resistance compounds with and without  $\beta$ -CDs. The results clearly indicated that  $\beta$ -CD application on textiles are quite complex. A greater loss of formaldehyde was noted, in addition to a lowering in the crease recovery angle due to crosslinking between DMDHEU and  $\beta$ -CD. The steric effects of the molecules come into play as well as the interference of β-CDs in the usual bond formation between chemicals and cotton fibres. MCT-\beta-CD can in fact be used as a formaldehyde free crosslinking agent in itself, since it has 2-3 reactive triazine groups per cyclodextrin molecule. Hebeish et al. reported on how easy-care characteristics can be achieved with a specific combination of MCT- $\beta$ -CD, resin and catalyst concentrations. Researchers report on how novel starches or scouring agents containing  $\beta$ -CDs can be used for sizing and bio scouring respectively. Within the laundry industry, CD present an opportunity to decrease the residual surfactants found on laundered fabric surfaces when added in the rinse cycle. MCT-  $\beta$  -CD finished polyester or polyester-cotton blend fabrics also have improved anti-static properties.

#### Fragrance release

Aromatherapy is increasingly popular as one of many approaches to healing with natural substances which are favoured by the public and make it possible for the individual to attempt self-therapy at home <sup>[9]</sup>. Various studies of the fragrance release properties of  $\beta$ -CD inclusion compounds have been conducted. The complexation of  $\beta$ -CDs with aroma molecules reduces their vapour pressure and delays the breakdown of the molecules due to photo degradation. Studies also show that using certain grafting agents with cyclodextrins (variables being the degree of grafting, type of cyclodextrin derivatives, and type of substrate and guest molecule) allows the fabrics to retain fragrances for longer periods of time, even so much as a year.  $\beta$ -CD cavities on the textile can also trap bad odours and these cavities can be emptied during the washing process. Empty cavities can be reloaded with padding, dipping or spraying or by keeping the moist cyclodextrin fabric in an atmosphere of the guest molecules at 50-60°C for a few hours. β-CDs are also known to stabilise the perfumes in washing powders for several days <sup>[6]</sup>.

#### Antimicrobial

Textiles have long been recognized as media to support the growth of microorganisms such as bacteria and fungi. The growth of microorganisms on textiles inflicts a range of unwanted effects not only on the textile itself but also on the wearer. Consumers' demand for hygienic clothing and activewear has created a substantial market for antimicrobial textile products <sup>[2]</sup>. There is an increased interest in the application of antimicrobial agents on textiles for healthcare and hygiene applications. Antimicrobial finishes on textiles generally consist of active antimicrobial components, either on the surface or within the fibres, that kill microorganisms

when they come in contact with them. Wang *et al.* incorporated an antimicrobial agent miconazole nitrate into the cavities of MCT- $\beta$ -CD <sup>[6]</sup>. The authors found that the antimicrobial agent incorporated into the fabric via cyclodextrin resulted in significant antimicrobial properties in comparison to the control fabrics. Butylparaben and Triclosan have also been used with cationic- $\beta$ -CD to provide antimicrobial properties to cellulose. The triazinyl group in MCT- $\beta$ -CD itself is a biocidal and can give some antimicrobial effects. Silver ions have also been loaded into cyclodextrin cavities to achieve an antimicrobial property.

### Others

Other guest molecules include sunscreen agents such as octyl methoxycinnamate, 4-hydroxy benzophenone, copper acetate molecules or zinc oxide nanoparticles, anti-mosquito repellent agents such as N, N,-diethyl-3-methylbenzamide and Permethrin for providing UV protection and mosquito repellence respectively. A flame-retardant  $\beta$ -CD complex incorporated into polyethylene terephthalate films for flame retardant function have also been tested. Furthermore, it is also suggested that biopolymers such as alginates, pectins, chitosan, etc. can be bound to textile fibres through  $\beta$ -CDs for the modification of textile surface behaviour. Inclusion compounds with semi fluorinated alkanes, such as already reported with  $\beta$ -CDs, could result in novel finishes such as biochemical protection finishes on textiles. Researchers also discuss the possible use of  $\beta$ -CD textiles for collecting diagnostic information from sweat. Table shows some common guest molecules along with their function on textiles <sup>[6]</sup>.

Guest molecule(s)	Application/ function	
Miconazole nitrate, Butylparaben and Triclosan	Antimicrobial activity	
Octyl methoxycinnamate, 4- Hydroxy benzophenone,	Sun screen agents	
Copper acetate molecules or Zinc oxide nanoparticles		
Permethrin, N, N, -diethyl-3- methylbenzamide (DEET), limonene	Mosquito Repellents	
Anti-blaze RD 1 (commercial flame retardant)	Flame retardants	
Lavender oil, citronella oil, vanillin	Fragrance properties	
Sweat	Trapping of bad odours & Diagnostic purposes	

## Toxicological properties of cyclodextrins

Given the fact that most of times the textiles get in touch with the human skin, it is necessary to know the toxicological properties of the substances applied on it before using them. Detailed studies of toxicology, mutagegicity, teratogenity and carcinogenity were carried out for the cyclodextrins and their derivatives. The results of these studies indicate that the cyclodextrins can affect the human organism only at extremely high concentrations. No acute intoxications have been noticed during the tests on animals. After the year 2000, β cyclodextrins were admitted in some countries as food additives (E 459) in the form of pellets and pills, with the restriction "only as necessary". They were also admitted as carriers or solvents for food additives, with the threshold of 1 g/kg. For textile finishing, the  $\beta$ -cyclodextrins modified with reactive groups (monochlorotriazinyl group) are used. This anchor- group reacts with the cellulose hydroxyl groups, forming permanent covalent bonds. In this case too, the toxicological data (for the cyclodextrin derivatives) are important. According to the OECD (Organization for Economic Co-operation and Development) tests, these cyclodextrin derivatives have no irritating or sensitization effects. Comparable results were also obtained for the textile products finished with this type of derivatives, these results being backed up by the first clinical tests with T-shirts, which detected no human skin irritations<sup>[3]</sup>.

### Conclusion

Cyclodextrins have the ability to form inclusion complexes with a large number of organic molecules; this property enables them to be used in a variety of different textile applications. As cyclodextrins can incorporate into their cavities different dyes, they could be used as auxiliaries in dyeing process. Regardless the mechanisms of cyclodextrins actions, if there is a competition for sites on the fibre between dyes and cyclodextrins; or cyclodextrins slow down the dyes migration by forming complexes with the dyes molecules which are released slowly to the fibre, cyclodextrins can act as levelling or retardant reagents in various textile fibre (cotton, polyester, polyamide, polypropylene, polyacrylonitrile) dyeing. In general, quality dyeing can be obtained and bath exhaustion can be improved when cyclodextrins are used as an additive (levelling reagent or retarding reagent) compared to commercially available auxiliaries; further improvement of colour levelness and some improvements in colour depth have been found when textile fibres were dyed in the presents of cyclodextrins. One of the main criteria for the complex inclusion is the size of cyclodextrins cavity and the size of the dyestuff molecules. The use of cyclodextrins in textile dyeing can not only improve the quality of the dyeing, but it can reduce the environmental impact of the exhausted baths. Further, covalently bonded cyclodextrins on textile support form inclusion complexes with organic pollutants. The adsorbed pollutants will be converted into water and carbon dioxide by the incineration.

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