APPLICATIONS OF β-CYCLODEXTRINS IN TEXTILES

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Abstract:

In this paper, the general features of β-cyclodextrin and their applications in the textile industry have been reviewed. The use of β-cyclodextrin in the textile industry is of great significance due to its wide range of application. One of the key aspects is the attachment technique of β-cyclodextrin to the textile's surface. This review deals with this in depth. Some quantification and characterization methods of Textile-β-cyclodextrin are discussed. In the last few years, the new direction in textile research is the functionalisation of textile systems. It is believed that β-cyclodextrin will play a very important role in these new developments. β-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. It is concluded that there are many possibilities for the development of new textile products with advanced properties based on β-cyclodextrin.

Key words:

β-cyclodextrin, textiles, functionalisation, complex inclusion, cyclodextrin cavity, host and guest molecules.

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 [1]. Since 2009, the total number of cyclodextrin related publications amounts to 42,000, with a daily average of 7 publications in 2009 (http://www.cyclolab.hu/services4.html), 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 α-1,4-glycosidic bonds. There are three types; α-cyclodextrin, β-cyclodextrin, γ-cyclodextrin, which are composed of 6, 7, and 8 α-1,4-glycosidic bonds as shown in Figure 1. 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 [2]. Solubilising is also said to occur through the formation of micellar types of aggregate in aqueous solutions [3]. The combination of β-CD and textiles to create new functionalised fabrics therefore received a lot of attention over the last decade.

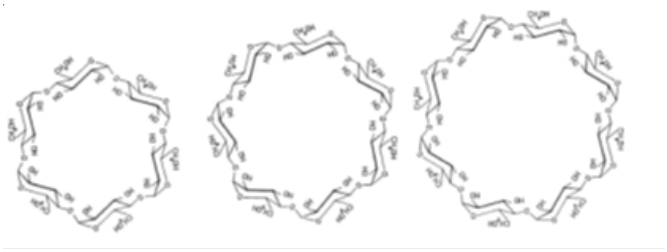

Figure 1. Structure of α-cyclodextrin, β-cyclodextrin, γ-cyclodextrin [4].

Research work mainly pertaining to β-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 β-CD in textiles, and this is of special interest to textile researchers working on adding functionality to textile surfaces. The role of β-CD as a treating and sizing agent has not been dealt with in this paper. β-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 β-CDs on textiles.

Preparation of β-CD and their complexes in free form

Around 30 different pharmaceutical products containing cyclodextrin are on the market. Some of the marketed drugs containing β-CD are listed in many review papers [2-3]. Various methods of complexation techniques are used, from solution, co-precipitation, dry mixing, extrusion, slurry method, kneading and grinding methods. Normally water is used as a solvent for complexation reactions. In cases where the guest molecules have a poor solubility in water, solvents such as ethanol and diethyl ether which do not complex well with cyclodextrin are used and are easily removed by evaporation [5].

Inclusion complexes are in fact energy favourable, since water molecules from the cavity are displaced by hydrophobic guest molecules to obtain an apolar-apolar interaction and decrease the cyclodextrin ring strain, thereby leading to a more stable lower energy state. The host guest complex is not a permanent feature and the longevity of the complex and the complexation strength depends on various factors such as the size of the guest molecule, the van der Waals interactions, the release of water molecules, hydrogen bonding, charge transfer interactions, hydrophobic interactions, and the release of conformational strain, etc [3].

Cyclodextrins such as β-CD do show limited solubility with lipophiles, sometimes resulting in the precipitation of complexes from water or other aqueous systems. In order to improve solubility, hydroxypropyl derivatives of β-CD, randomly methylated β-CD, and branched cyclodextrins are used. The

enhanced solubility in derivatives is due to the transformation of the crystalline cyclodextrin into the amorphous mixtures of isomeric derivatives [6]. Normally a 1:1 complexation ratio is found between the drug and the cyclodextrin molecule, while sometimes 1:2 or 2:1 is also found [3]. Disassociation of such complexes is driven by the increase in number of water molecules in the surrounding environment [5].

Once a formed complex is placed in water, the complex dissolves and the guest molecules are displaced by water molecules and equilibrium is reached between the free and complexed cyclodextrin and the guest, and the dissolved and undissolved complex.

General industrial applications of β-CD

Typical pharmaceutical drug release profiles are of four main types; immediate, prolonged, modified and delayed [7]. Based on this knowledge, cyclodextrin derivatives are used in the pharmaceutical industry to modify drug release. For instance, by altering the disassociation equilibrium towards complexation a sustained release effect can be obtained.

Apart from applications in the pharmaceutical industry, β-CD has found applications in the cosmetic industry in the controlled release of fragrances from inclusion products, such as from detergents, perfumes and room fresheners. Other applications in personal care products include toiletries, toothpastes, skin creams and dusting powders. In the food industry (generally the largest industry consumers of β-CD), β-CDs are used to remove cholesterol from milk, butter and eggs, as well as for food preservation. They are also used for flavour protection and flavour delivery [1]. They also have applications in the agro industry through complex formations with pesticides, herbicides, insect repellents, etc [1-2, 5]. In environmental sciences, β-CD is used in the removal of organic pollutants and heavy metals from water and soil [7-9].

β-CD and textiles

β-CD can be incorporated onto textile by means of spraying, printing, padding, grafting, surface coating, impregnation, ink jet printing or via sol gel, etc [10-13]. Table 1 shows the various feasible interactions between β-CD and some textile fibres.

Table 1. Feasible interactions between β-CD and some textile fibres [14].

Parameter	Cotton	Wool	PES	PA	PAN	PP
Ionic interactions	-	+	-	+	+	-
Covalent bonds	+	+	-	+	-	-
Van der Waal forces	-	-	+	+	+	-
Crosslinking agents	+	+	+	-	-	-
Graft polymerisation	+	+	+	+	+	+

+=possible,-=not possible, PES-polyester, PA-polyamide, PAN-polyacrylonitrile, PP-polypropylene.

Fixation of β-CD onto textiles

Listed in the literature among various mechanisms to fix β-CD to fibres, a large volume of them are on grafting with the use of crosslinking agents such as polycarboxylic acids onto cotton [11-13], wool [12-13], polyester [13, 15-16], polyamide [17] and polyacrylonitrile fibres, etc among others [18]. The crosslinking mechanism of crosslinking agents, such as 1,2,3,4, butanetetracarboxylic acid (BTCA) as shown in Figure 2, is through the formation of a five member anhydride intermediate [19]. This reacts with the hydroxyl groups of cellulose and/or β-CD through esterification, as shown in Figure 2. Therefore, citric acid acts as a crosslinking agent providing cotton with anti wrinkle properties, and it also connects β-CD to cotton.

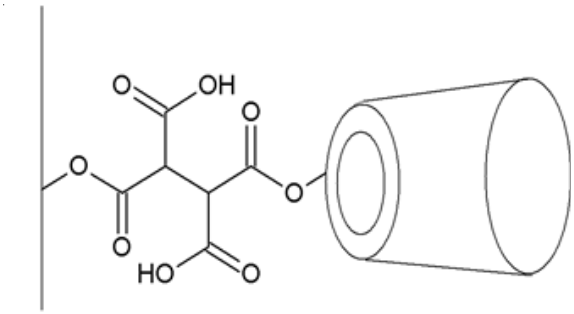

Figure 2. Grafting of β-CD via 1,2,3,4, butanetetracarboxylic acid (BTCA) onto a cotton textile [11].

Resins such as epicholorohydrin can also be used to fix β-CD to cellulose [20-21]. The use of butyl acrylate for the grafting of the monochlorotriazinyl derivative of β-CD (MCT-β-CD, shown in Figure 3) to cellulose fibres is mentioned [22], and in another case the grafting of glycidal methacrylate of β-CD or MCT-β-CD to polyamide fibres [23] or the same to β-CD and polypropylene is discussed [20].

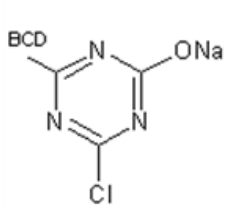

Figure 3. Structure of monochlorotriazinyl functional group of MCT-β-CD molecule [24].

MCT-β-CD can be used to permanently bind β-CD to cotton with the conventional reactive dyeing method [25-26]. 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 [27], as shown in Figure 4. Different substituents (such as siloxanes, alkyl amines, polyethylene glycols, etc.) for β-CDs with absorptive properties can be obtained from MCT-β-CD, which can be attached through electrostatic or hydrophobic interactions [28]. β-CDs can be covalently connected via heterobifunctional reactive dyes which contain monochlorotriazine and vinyl sulphone groups [29].

Non-ionic β-CD derivatives can be fixed to hydrophobic textiles (such as polyamide, polyester and polyacrylonitrile) via the disperse dyeing method through hydrophobic interactions, and cationic β-CD derivatives can be fixed to, for instance, polyacrylonitrile under basic dyeing conditions [26].

β-CD and their derivatives can also be added to a synthetic pellet melt mixture [30-31] in addition to being electrospun into nanofibers with polymers such as poly methyl methacrylate [32]. Fixing of β-CD via the sol gel process has also been done with the use of tetraethoxysilane and 3-Glycidyloxypropyl-

Table 2. Table of some of the different β-CD fixation techniques to textiles.

Technique	Material	Cyclodextrin type	Chemical used	Common reaction conditions & steps with fabric	Reference
Crosslinking	cotton, wool, polyester, polyamide, polyacrylonitrile	β-CD	Polycarboxylic Crosslinker (BTCA, citric acid)	β-CD + BTCA with catalyst sodium hypophosphite, fixation for 170ºC for 3 min & pH 2.7	[11-13, 15-19]
	cellulose (cotton)	β-CD	Epichlorohydrin	Swollen cellulose in alkaline conditions for 2.5 h at 60ºC	[20-21]
	cotton	β-CD	Reactive dyes (home & heterofunctional dyes)	Dye +electrolyte+ β-CD for 15 min. at 40 º C+ $NaCO_3$ for 10 min. at 50ºC and fixation with NaOH for 45 min.	[29, 35]
Grafting	cotton	MCT- β-CD	Butyl acrylate (BuA) & Potassium persulphate (KPS) as initator	Step 1: Polymerisation- MCT-β-CD + BuA+KPS for 3 h at 65ºC & continued for 18 h at 30ºC, washed in ethanol and dried in acetone at 50ºC Step 2: Padding at different pH & temp.	[22]
	polyamide	MCT- β-CD/ β-CD	Glycidal Methacrylate (GMA) & Potassium persulphate (KPS) & Copper sulphate (CuS)	Fabric + 3 % solution of KPS for 20 min., washed & dried + GMA+CuS+ 3 drops of detergent for 75ºC for 1 h and washed + β-CD + NaOH mixed at 80ºC.	[20, 23]
	polypropylene	β-CD			
	cotton/tencel	N-methylolacrylamide β-CD (NMA- β-CD)	Cerium ion	ceric ammonium nitrate+1% HNO_3 for 20 min + NMA- β-CD in Ar atmosphere for 40 min.	[20, 36]
Reactive fixation	cotton/tencel	MCT- β-CD	NA	MCT- β-CD +$NaCO_3$, oven cured for 5- 15 min. at 130-170ºC.	[18,22-23,32,46,53-54]
Disperse dyeing method	polyamide, polyester and polyacrylonitrile	Non-ionic β-CD derivatives	NA	pH=4-6, 130ºC	[26]
Basic dyeing method	polyacrylonitrile	cationic β-CD derivatives	NA	2ºC/min till 80ºC and 0.7ºC till 75ºC treatment time=80 min. liquid to cloth ratio=1:50	[26]
Electrospinning	poly methyl methacrylate	β-CD	NA	PMMA + β-CD in 1ml 0.4 mm diameter needle syringe, feed rate 1-4ml/h, 10-20 kV, tip to collecting distance=10-20 cm	[32]
Sol gel process	cotton	β-CD	tetraethoxysilane (TEOS)and 3-Glycidyloxypropyl-trimethoxysilane (GPTMS)	Step 1: sol gel solution preparation-TEOS+GPTMS emulsified for 15 min. at 500 r.p.m and then shaken for 8 h at 40ºC. Step 2: β-CD is added & fabric is wet padded.	[33]
Enzymatic coupling	cotton	Tyr- β-CD	tyrosinase	Step 1: Aminisation of cotton - Dyeing cotton with a homofunctional dye with amine groups such as RB 5 and subsequently reducing it with sodium hydrosulphite for 2 h at 80ºC. Step 2: Attachment to fabric-Tyr - β-CD is hydroxylated with tyrosinase and attached to fabric at pH 7.5 at room temp. for 2 h by immersion.	[35]
Polymer extrusion	polyethylene terephthalate, polyamide	β-CD	NA	1:1 mixing of pellet powder with β-CD	[30-31, 37]

β-CD- β-cyclodextrin, TEOS- Tetraethoxysilane, GPTMS- Glycidyloxypropyl-trimethoxysilane, Tyr- β-CD- Tyrosinase β-cyclodextrin, MCT- β-CD- Monotriazinyl β-cylcodextrin, NMA- β-CD- N-methylolacrylamide β-cyclodextrin, BTCA-1,2,3,4, butanetetracarboxylic acid , KPS- Potassium persulphate, BuA- Butyl acrylate, NaOH- Sodium hydroxide, $NaCO_3$ –Sodium carbonate, HNO_3 -Nitric acid, NA-not applicable.

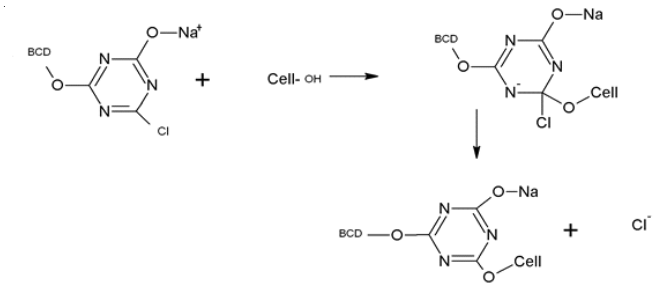

Figure 4. Attachment of MCT-β-CD to cotton [34].

trimethoxysilane [33]. Table 2 shows the various fixation techniques to used to secure β-CD to textile fibres, with a brief mention of some of the reaction conditions.

Newer fixation methods

In addition, newer methods of fixing β-CDs include the use of homobifunctional reactive dyes such as Reactive Black 5. The attachment of β-CD with homobifunctional reactive dyes can be done in a one step process with the β-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 β-CD and to the cotton surface compared to that of a heterobifunctional reactive dye [35].

Another new method of attachment is β-CD derivative attached to the tyrosyl group (Tyr-β-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)-β-cyclodextrin through the IUPAC nomenclature. 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-β-CD, as shown in Figure 5. Agrawal et al. [35] note that fixation with homobifunctional dye and with Tyr-β-CD result in higher amounts of β-CD on the fabric compared to any other method, including attachment of tyrosinase mediated Tyr-β-CD to a non reduced reactive dyed fabric.

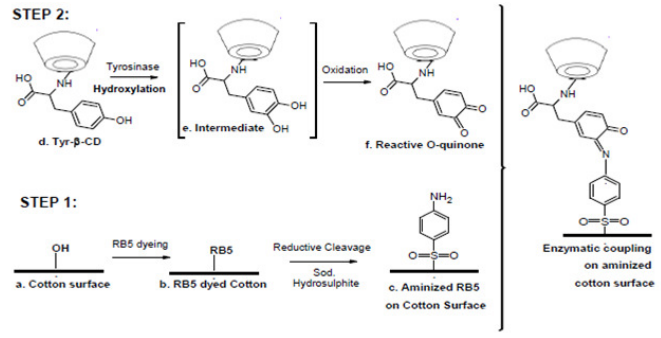

Figure 5. Schema of attachment of Tyr-β-CD to a functionalised cotton textile [35].

Characterisation and Quantification of bound β-CD

Direct measurements of MCT-β-CD on cotton can be conducted with reflectance or absorbance measurements in the UV region by a spectrophotometer, or simply by a gravimetric method [26]. Among several dye related methods enlisted to quantify bound β-CD on fibres, phenol red, phenolphthalein, methyl orange indicator, etc. have been suggested, in addition to using iodine vapour for spectrophotometer measurements [20, 26]. The use of fluorescent dyes such as 1-anilinonaphthalene-8-sulphonate, dansyl chloride and dansyl leucine, as well as 2-p-toluidinyl-napthalene-6-sulphonic acid and o-anisaldehyde, etc., have been mention for quantification purposes [1]. To characterise MCT-β-CD cellulose or regenerated cellulose fibres fixed with MCT-β-CD, triaine tests and elemental analysis with reference to the nitrogen content, such as the Kjeldahl method, have been documented [20, 38-39]. The use of a volatile amine such as cyclohexylamine for the determination of the amount of accessible cyclodextrins available for inclusion has also been described in the literature [40]. Among the characterisation tests, the use of FTIR, XPS analysis and X-ray fluorescence analysis is reported by Sricharussin et al. [41], Kistamah et al. [24] and Bereck [42] respectively. New analytical methods are being developed to directly determine the binding of β-CD, such as with ferrocene dye which builds 1:1 stable complexes with β-CD [42-43].

End applications of β-CD in the textile industry

Textile processing

There is a vast amount of literature on the influence of β-CDs on dyeing. It has been reported that β-CDs can absorb dyes [44] 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 [20, 25, 45]. For instance, dyeing of cotton-polyester blends with disperse dyes and β-CDs led to an improved dye strength and deeper dye shades [46]. Disperse dyeing of cellulose acetate treated with β-CD showed similarly improved colour intensity as well as the possibility of dyeing at lower temperatures than conventionally used [47]. β-CD can also act as retardant with dyes with which it can form complexes [48]. 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 [49]. Dyeing and easy care finish can be achieved by using a formulation containing a reactive dye, MCT-β-CD and a resin.

Dimethyloldihydroxylethyleneurea (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 β-CDs [50]. The results clearly indicated that β-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 β-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-β-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 [51]. Hebeish et al. [38] reported on how easy care characteristics can be achieved with a specific combination of MCT-β-CD, resin and catalyst concentrations. Researchers also report on how novel starches or scouring agents containing β-CDs can be used for sizing and bioscouring respectively [52-53].

Within the laundry industry, cyclodextrins present an opportunity to decrease the residual surfactants found on laundered fabric surfacse when added in the rinse cycle. MCT-β-CD finished polyester or polyester-cotton blend fabrics also have improved anti-static properties [39]. Currently there are two commercial textile auxillary products; Cavasol® and Febreze® by Wacker Chemie AG and by Proctor & Gamble respectively [54].

Fragrance release

Various studies of the fragrance release properties of β-CD inclusion compounds have been conducted [13, 41, 55-57]. The complexation of β-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 [13]. β-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 [20, 36, 41] or by keeping the moist cyclodextrin fabric in an atmosphere of the guest molecules at 50-60ºC for a few hours (vapour method) [13, 58] . β-CDs are also known to stabilise the perfumes in washing powders for several days [1].

Antimicrobial

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. [59] incorporated an antimicrobial agent miconazole nitrate into the cavities of MCT-β-CD. 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-β-CD to provide antimicrobial properties to cellulose [60]. The triazinyl group in MCT-β-CD itself is a biocidal and can give some antimicrobial effects [23]. Silver ions have also been loaded into cyclodextrin cavities to achieve an antimicrobial property [61].

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 (DEET) and Permethrin for providing UV protection and mosquito repellence respectively. The structures of some guest molecules are shown in Figure 6. A flame retardant β-CD complex incorporated into polyethylene terephthalate films for flame retardant function have also been tested [37].

Table 3. Table of guest molecules and their functions.

Guest molecule(s)	Application/ function	Reference
Miconazole nitrate, Butylparaben and Triclosan	Antimicrobial activity	[59, 61]
Octyl methoxycinnamate, 4-Hydroxy benzophenone, Copper acetate molecules or Zinc oxide nanoparticles	Sun screen agents	[19, 46, 65]
Permethrin, N, N, -diethyl-3-methylbenzamide (DEET), limonene	Mosquito repellents	[66-68]
Anti-blaze RD 1 (commercial flame retardant)	Flame retardants	[37]
Lavender oil, citronella oil, vanillin	Fragrance properties	[13, 29, 41, 55-57]
Sweat	Trapping of bad odours & Diagnostic purposes	[62, 64]

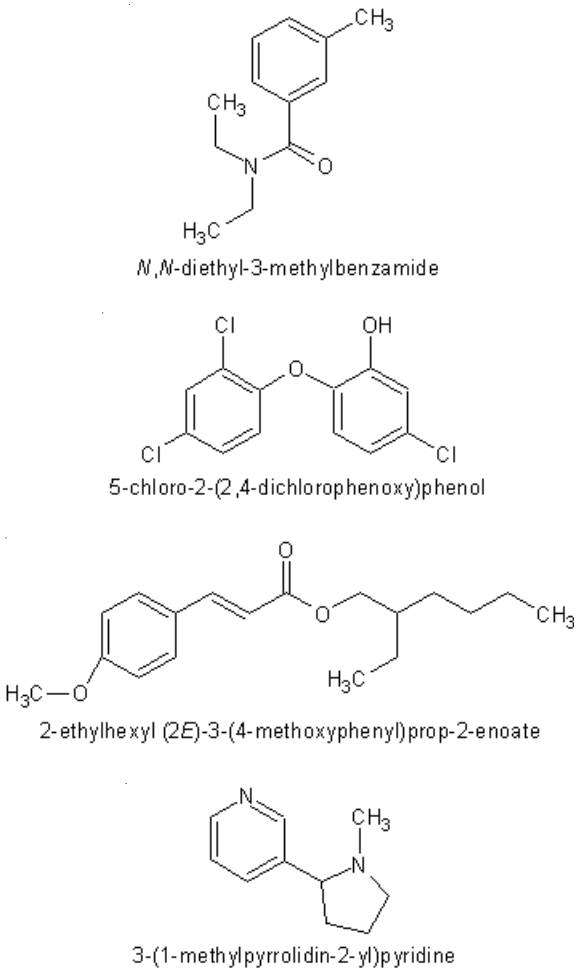

Figure 6. Examples of guest molecules. a) N, N,-diethyl-3-methylbenzamide (DEET) b) Triclosan c) octylmethoxy cinnamate d) Nicotine.

Furthermore, it is also suggested that biopolymers such as alginates, pectins, chitosan, etc. can be bound to textile fibres through β-CDs for the modification of textile surface behaviour [62]. Inclusion compounds with semi fluorinated alkanes, such as already reported with β-CDs, could result in novel finishes such as biochemical protection finishes on textiles [63]. Researchers also discuss the possible use of β-CD textiles for collecting diagnostic information from sweat [62, 64]. Table 3 shows some common guest molecules along with their function on textiles.

Characterisation and quantification of guest molecules

In general, NMR is recommended for the study of the complex formation. In the case of coloured guest molecules, a UV spectrophotometer is used. The kinetics of the release of guest molecules in pure water as a function of time can also be studied using a UV spectrophotometer [23]. The UV spectrophotometer measurement of fabrics can be carried out where possible [53, 55, 61]. Szejtli [1] lists different methods for determining guest content such as X- ray powder diffraction, thin layer chromatography, evolved gas analysis, etc. Other analysis include FTIR spectroscopy, thermogravimetric analysis, differential scanning calorimetry [1, 69] as well as Raman spectroscopy which is said to uniquely identify the inclusion complex [43].

Gas chromatography-microscopy chromatograms was used by Srichaurussin et al. [41] to characterise the complexed aroma molecules. The use of gas chromatography to analyse the sweat complexed in cyclodextrin cavities for diagnostic purposes has also been conceptualised [41, 64]. For the characterisation of octyly methoxycinnamate as a guest molecule, Scalia et al. [65] used thermogravimetric analysis, high pressure liquid chromatography after soxhlet extraction. The authors also used transpore assay to quantify the UV protection factor obtained from using a sunscreen guest molecule. For the measurement of antimicrobial effects, several methods exist such as the agar diffusion plate test, suspension method, etc. [70]. Researchers working with insect repellents [68] tested the effectiveness of the anti mosquito guest molecules using an mosquito bio assay.

Conclusions

β-CDs play an important role in innovative textile processing and the functionalisation of textiles, both of which currently hold the increased interest of textile researchers. The uses of β-CDs provide immediate opportunities for developing new innovative products and eco friendly textile processes which are of specific interest to the textile industry. From the wide spread of industrial applications as auxiliaries, β-CDs also have a great potential in newer applications in the area of medical and technical textiles. Currently, newer methods of attachment of β-CDs, such as Tyr-β-CD, are being developed and applied. Newer methods in the quantification of the attached β-CDs on textiles are being developed with dyes such as ferrocene. In conclusion, it can be stated that there are many possibilities for the development of new textile products with advanced properties based on β-CDs. Furthermore, though the introduction of new viable β-CDs in applied industrial methods and applications may take time, they are not far on the horizon.

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