



Review Article

New Textile Applications of Cyclodextrins

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Abstract

New areas of applications of cyclodextrins with textiles are possible. The ability of cyclodextrins to form inclusion complexes can be used, e.g., to remove malodor from textile materials. The permanent fixation of cyclodextrins offers new textiles with interesting properties. Thus the formation of body odor is reduced by the complexation of the organic compounds of sweat. The release of perfumes from cyclodextrins is possible by the use of textiles with fixed cyclodextrins. Pharmaceutical compounds are also set free in contact with the skin. Last but not least the analysis of the different compounds of the human sweat complexed by the cyclodextrins offers new possibilities in medical diagnostics.

Introduction

Cyclodextrins (CDs) are polysaccharides built from six to eight ($\alpha = 6$, $\beta = 7$, $\gamma = 8$) D-glucose units and are formed during the enzymatic degradation of starch. The D-glucose units are covalently linked at the carbon atoms C₁ and C₄. More than 100 years ago cyclodextrins were mentioned in the literature by Villiers [1] and also a little later by Schardinger [2]. At this time nothing was known about the structure of these molecules (Figure 1).

It took more than 50 years before Cramer described the possibility of the formation of inclusion compounds with cyclodextrins [3]. At this time the idea of the formation of neutral complexes with cyclodextrins and other neutral molecules was revolutionary. No interactions between charged or polar molecules take place during the formation of cyclodextrin complexes. This idea was quite exceptional at that time and as a result it was rejected by some prominent scientists [4]. In a lecture given at the First International Symposium on Cyclodextrins Cramer describes this situation: 'A whole mafia of physicochemists was united against the young greenhorn from Heidelberg. I believe the concept was finally successful.' [5]. Nowadays no one is surprised about the formation of neutral cyclodextrin complexes with neutral guest molecules.

For many years cyclodextrins were only available in small quantities. Thus no practical applications seemed to be suitable for these molecules. However, in 1980 Saenger published a review article about cyclodextrins [6] in which he mentioned some industrial applications. The First International Cyclodextrin Symposium organized by Szejtli took place in Budapest in 1981 [7]. One year later the first cyclo-

dextrin book written by Szejtli was published [8]. Since this time a general interest in cyclodextrins and their possible applications exists, with the number of publications and patents increasing annually.

Pharmaceutical applications of cyclodextrins have been mainly described in the literature [9–12]. A few applications in food and cosmetics are also known [12]. The price of the cyclodextrins was mainly responsible for the relatively low number of practical applications. Fortunately during the last few years prices have decreased and therefore further applications of cyclodextrins have become possible.

The use of cyclodextrins in textile processes was reviewed some years ago [13]. During recent years further textile applications of cyclodextrins have been developed. In this paper some new applications of cyclodextrins with textile products will be reported.

Toxicological properties of cyclodextrins

Due to the fact that textiles are mainly in contact with human skin, the toxicological properties of cyclodextrins must be known for these applications. Detailed studies of the toxicity, mutagenicity, teratogenicity and carcinogenicity of cyclodextrins and some of their derivatives have been performed [14]. These results indicate that cyclodextrins may be harmful to the human organism only at extremely high concentrations. No indication of an acute toxicity was observed during animal experiments [6].

Since November 13, 2000 β -cyclodextrin is licensed in Germany as an additive in food [15]. β -Cyclodextrin was included as a food additive (E 459) in the form of tablets and dragees with the limitation 'as much as necessary'. It was

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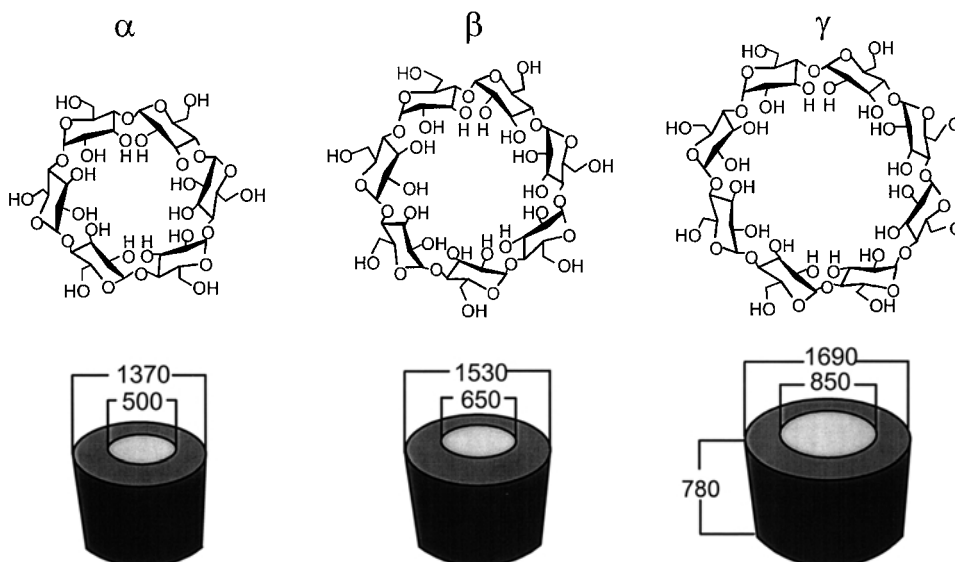


Figure 1. Chemical structure of cyclodextrins (dimensions in pm).

Table 1. Toxicological data of the β -cyclodextrin derivative with a monochloro triazinyl group [26]

Test	System	Result
Acute oral toxicity (OECD No. 401)	rat	LD50 > 2000 mg/kg
Primary skin irritation (OECD No 404)	rabbit	not irritating
Skin sensitisation (OECD No 406)	guinea pig	not sensitising
Amestest (OECD No 471)	Salmonella typhimurium	not mutagenic

also licensed as a carrier or as a solvent for additives of food with the limitation of 1 g/kg.

For use in textile finishing, β -cyclodextrin modified with a reactive group (monochlorotriazinyl group) is used. This anchor group reacts with the hydroxyl groups of cellulose and the cyclodextrin is permanently covalently bound. Therefore also toxicological data for this cyclodextrin derivative are important. Some of these data are summarized in Table 1.

According to the OECD tests this cyclodextrin derivative has no irritating or sensitising effects. Thus comparable results for textile materials finished with this derivative are expected. These expectations are supported by the first clinical trials with T-shirts. No irritation of the human skin could be detected [16].

Uses of cyclodextrins in connection with textiles

Two fundamental possibilities have to be distinguished:

(I) There are no chemical or physical interactions between cyclodextrin and the textile materials.

In this case cyclodextrins or their complexes are used to positively influence the quality of use. It is known that cyclo-

dextrins form complexes with perfumes or fragrances which can be stored over a long period without loss of these substances. The complexed organic substances are only set free in contact with moisture. Thus it is possible to add a fresh smell in a drier to just washed laundry using cyclodextrin complexes [17, 18]. The fragrance complexed inside the cavity of the cyclodextrins is activated by the moisture in the drier. Cyclodextrin complexes with fragrances and perfumes are stable over a long period and may therefore also be used in washing powder and other products for the cleaning or care of textiles [19, 20].

On the other hand unpleasant odours of textiles can be removed by the complexation with cyclodextrins. Spraying such a textile with a solution of cyclodextrins results in complex formation with the substances responsible for the unpleasant odour [21, 22]. No interactions between these complexes and the textile materials take place. As a result the complex is removed from the surface by mechanical stress. For example, during the cleaning of carpets the solid complex is removed together with dirt particles. Afterwards the textile material is completely odourless again because the unpleasant odour was removed not masked. Cyclodextrins or their complexes remaining are very soluble in water and they are at least removed from the textile material with the next washing.

(II) There is permanent fixation of cyclodextrin on the fibre surface.

Another possible use of cyclodextrins results from the permanent fixation on different polymeric materials [13, 23–25]. Cyclodextrin derivatives with a reactive group, e.g., the monochlorotriazinyl group [26, 27] (Figure 2) are able to react with the hydroxyl groups of cellulosic fibres like reactive dyes. Permanent fixation on fibres made from polyester is only possible with cyclodextrin derivatives with long alkyl chains or other hydrophobic groups (Figure 2). Comparable with disperse dyeing, the hydrophobic part of the substituted cyclodextrins migrates into the fibre above the glass transition temperature. The polar cyclodextrin molecule remains

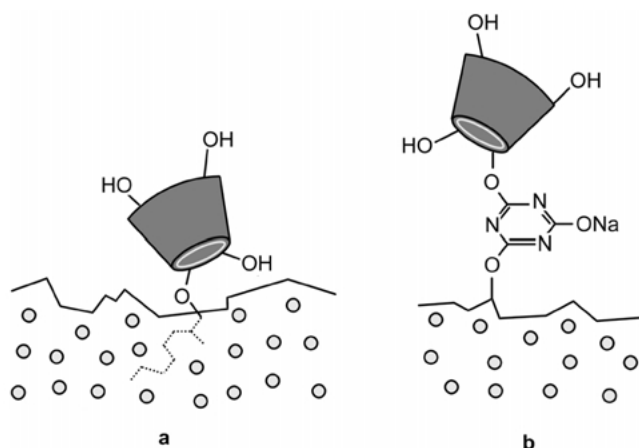


Figure 2. Schematical presentation of the fixation of cyclodextrin derivatives with hydrophobic (a) or reactive groups (b) on a polymer surface.

on top of the fibre surface. The polar hydroxyl groups of the cyclodextrins prevent the migration of the cyclodextrin molecule itself into the polyester fibre. Now the cyclodextrins cannot be removed by washing from the surface of the fibre. They are still able to complex organic substances resulting in different possible uses:

1. Cyclodextrins fixed on textile materials are able to complex substances into the empty cavities e.g., organic molecules from sweat. Therefore the possible formation of malodor is prevented. The odor from sportswear soaked with sweat is reduced or does not smell at all, if cyclodextrins are present on the textile. The same is valid for socks or other textiles used directly in contact with the body.

However, the cleaning of textiles with cyclodextrins is as necessary as for textiles without cyclodextrins. Only the comfort of wearing is positively influenced by the cyclodextrins.

2. Before wearing textile with attached cyclodextrins the cavities may be filled with perfumes. This is possible during the drying of the textiles after washing or even later, just by spraying with a perfume. The perfume molecules encapsulated in the cyclodextrin cavities do not evaporate. These molecules are stored over a long period of time. Small amounts of water as they are set free from the skin are essential for the release of the perfume molecules. In practice a blouse or scarf will start smelling only when they are near to the skin. Simultaneously organic substances from sweat are complexed.

Further applications are towels which start smelling by drying one's hands. Also bed linen may release a pleasant odor after going to bed. Curtains with cyclodextrins can be used to improve the air in rooms or offices with smokers. One should use one's fantasy to find more applications.

During the cleaning process of these textiles the residual perfumes or other organic substances complexed during use are removed. Afterwards the reloading of the cyclodextrin cavities with perfumes or other organic molecules is possible again. Thus the user of these textiles individually decides about the scent set free from their clothes.

3. The complexation or release of substances by fixed cyclodextrins can also be used for medical applications [28].

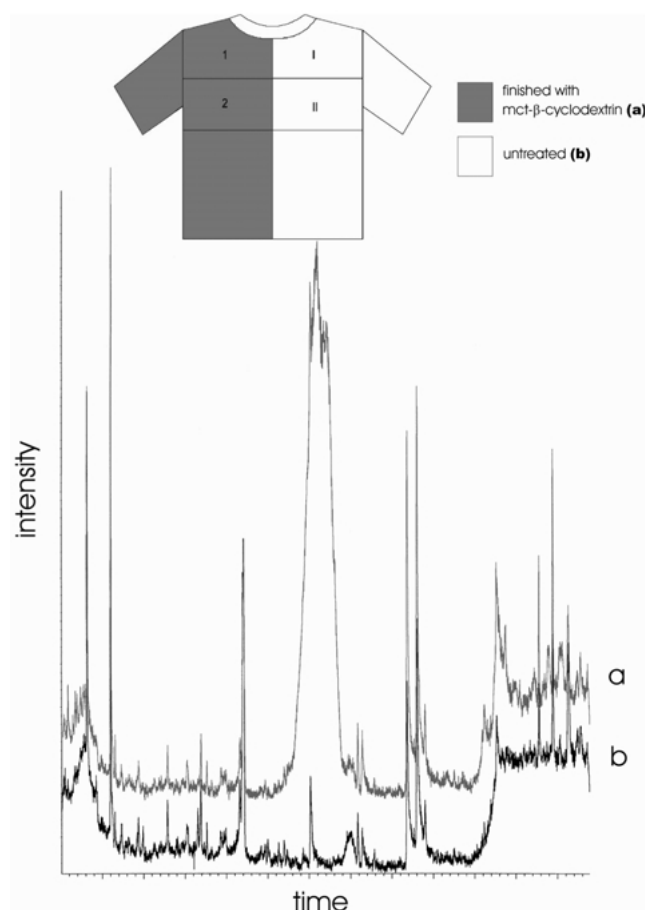


Figure 3. Schematical sketch of a T-shirt partially finished with (a) and without cyclodextrins (b) and used for 24 hours and the gas chromatograms of the corresponding extracts.

The identification of the organic compounds from patients enables new methods in medical diagnostics. Up to now blood or urine tests are normally used due to the problems of taking a sweat probe from a patient. This becomes easy by wearing textiles with cyclodextrins (Figure 3). After extraction of a textile with and without fixed cyclodextrins more substances are detectable using gas chromatography from the part with cyclodextrins [29]. The complexation of organic substances from sweat results in a preconcentration and the identification becomes easier.

Pharmaceutically active substances are complexed by fixed cyclodextrins. They are set free by wearing and can penetrate into the skin [28]. In this way the treatment of extensive skin diseases is simplified.

Conclusions

The fixation of cyclodextrins on textile materials leads to new quality of uses. It is not possible to describe all applications one may think about. The use of cyclodextrins together with textiles opens new opportunities for cyclodextrins.

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