APPLICATIONS OF CYCLODEXTRINES IN TEXTILES – A REVIEW

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Abstract. The cyclodextrin capacity to form inclusion complexes is known for a long time, this property being used in textile industry to obtain products with applications in increasing wear comfort and realization of medical textiles. Yet, there is always the possibility to find new applications of these complexes, either by their permanent fixation on textiles, or by making them environmentally friendly and increasing the performances of some processes from the textile industry or waste water treatment. What concerns the increase of wear comfort, the cyclodextrins serve to improve the wettability and antistatic properties, by catching the smells and perspiration, or to release for a long time the previously encapsulated perfumes. In the medical area, with a view to obtain a slow release of the antibiotics and based on the cyclodextrins capacity to form reversible inclusion complexes with them, operational vascular prostheses were created, which diminish the hazard of post-surgery infections. Based on the same principles, trans-dermal treatments were carried out, for example the realization of a bandage able to release natrium diclophenac as an anti-inflammatory medicine. The cyclodextrins are also used to release disinfecting or cicatrizing substances at the place were bandages are applied to cure various injuries, and for the realization of textiles with anti-microbial activity which resists to a number of washings. In the field of textile chemical technology optimization, the cyclodextrins are used to remove the surfactants from the

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material or to inactivate them in liquid phase, to intensify the enzyme processes or as balancers in dyeing with reactive pigments.

**Key words:** cyclodextrin, diclophenac, inclusions, monochlorine-triazynil, bandages, prostheses.

1. Introduction

This literature synthesis proposes to review the most important accomplishments from the last years in the field of cyclodextrins (CD) applications on textiles and especially in the field of medical textiles.

The cyclodextrins (also called Schardinger dextrins, cycloglucose, cycloamylose, cycloglucoamylose) are non-reducing cyclical oligo-saccharins, consisting of 6 to 12 (sometimes even 26) α-D (+)-glucopyranosic groups bound to α-1,4 glycosidic. Due to its specific molecular structure, with internal lipophylic cavities and external hydrophilic surfaces, the main property of CDs consists in their capacity to include various guest molecules, such as: polar compounds (amines, acids, esters, etc), aliphatic and aromatic hydrocarbons, rare gases, oxygen, carbon dioxide and even polymers (Grigoriu, 2009).

At more than one century after they were discovered, the cyclodextrines are among the mostly used host molecules utilized in the supra-molecular chemistry, widely applied in pharmacy, cosmetic industries, food technology, agriculture, stock raising, etc.

Their main advantages are:
- accessibility and capacity of continuous natural regeneration of the basic material (starch);
- relatively simple ecological preparation, at an accessible cost;
- multiple possibilities of synthesis of some inclusion complexes and of CD based derivatives, having a minimum toxicity (Grigoriu, 2009).

The necessity of a study in this field resides in the multitude of published papers having the cyclodextrin as a subject, simultaneously with the diversification of the types of products that make use of these compounds, imposing a series of requirements, such as: pre-established and reproducible physical-chemical properties, correlated with the field of application, mild non-polluting processing conditions, low energy consumption, diminished waste amount.

Taking into account the increasing demand on the world textile market and the dynamics of extension of highly performing smart materials, the study of textile materials amelioration remains still an open gate for new confrontation, with new possibilities of realization, application and interpretation. In this context, this review represents an attempt to systemize the information reported in literature, by approaching some aspects connected with the applications of cyclodextrin inclusion complexes in the textile industry, enabling the specialists
to use the new scientific reports in order to adapt the characteristics of the textile substrate to the performances imposed by the end destination.

A topic represented quite well in literature is that of anti-microbial agents’ incorporation in the textile fibers, these agents having to resist repeated washing and to provide septic conditions in various situations of textile material applications (hospital environment, patients with various skin diseases with super-infection hazard, etc.) (Wan & Cai, 2008).

Part of authors have analyzed the cyclodextrin problems without making reference to textiles; for example, treated the problem of essential sage oils micro-encapsulation (Tian et al., 2008). Yet, taking into account the possibility that this information can be used by textile specialists, the paper was also included in this review. It mainly deals with the proposed methods of encapsulation, the analysis of the factors that influence this phenomenon and the analysis of the stability of the formed complexes, all these being also valid in case that this type of substances are applied on textiles.

In order to shed light on some aspects concerning the manner of cyclodextrin bonding on the textile material, reference was made to papers that analyze this phenomenon in details in the case of making it functional with monochlorotriazynil, the resulted complex behaving like a reactive dye in relation with the cellulose support (Hebeish & El-Hilaw, 2001). Other investigation methods have also been presented for the reaction of monochlorotriazynil- β- cyclodextrin derivatives (MCT-β-CD) at the surface of cellulose materials, tencel and bleached cotton, such as X-rays photo-electron spectroscopy (Kistamach & Carr, 2006).

The factors with influence on the formation and decomposition of inclusion complexes, very important for the utilization of especially versatile complexes, as well as for the selection of the cyclodextrin type (α, β, γ or δ), constitute the object of several studies and are of special interest for medical textiles with slow medicine release. There have been also analyzed the influence of the size of cyclodextrin cavity on the possibility to integrate large molecules with various polarizations, as well as the influence of temperature, preparation method, the additive presence, the pH value, dilution etc. on the medicine/cyclodextrin balance, as well as the factors of influence on the trans-dermal permeability, very important for the utilization of cyclodextrins grafted on textiles, in view of topical administration of medicines (Challa et al., 2005).

Another important application in textile products finishing is cyclodextrin utilization as dye equalizer (Perrin et al., 2007). Given their polar interior and hydrophobic exterior, the cyclodextrins have the capacity to form complex inclusions with dyes in aqueous medium. The cyclodextrins equalizing and retarding effects has been experimentally proven when dyeing, for example, the polyamide 6,6 with acid dyes, when an increase of the critical dyeing temperature and an uniformity improvement were found.
The cyclodextrins grafted on textiles have also found applications in the waste water treatment. It is well known that the textile products finishing is water polluting activity. At the same time, the filters on textile support, especially on unwoven support, with grafted cyclodextrins, represents a solution for water purification (Crini & Morcellet, 2002). The polypropylene materials are especially adequate due to their chemical inertia, even in very corrosive mediums, taking into account that the problem of cyclodextrins grafting on polypropylene by using an activating electron beam (Crini & Morcellet, 2002) was already solved.

By analyzing the papers from the scientific publications appeared during the last decade, one can notice the interest of scientists from different fields, for both cyclodextrins and their derivatives. Very diverse applications were found for these complexes, and only in the textile domain which constitutes the subject of this review, the variety of applications leads to the necessity of a classification from this standpoint. Therefore, to simplify the things, the field of cyclodextrins utilization in textiles could be divided in five groups:

- environmental protection and increase of the performances of some technological processes in the textile industry;
- improve the wear of textile products (fabric hand, anti-allergic properties, etc);
- applications in medical textile field (with antimicrobial properties, for trans-dermal treatments, as prostheses with antimicrobial action, support for cell growth, etc);
- realization of anti-insect textile products;
- waste water treatment.

This classification was set at the basis of the present review, yet considering from the beginning the necessity to explain some general mechanisms of inclusion product generation and guest release, then the factors that influence these phenomena.

2. Cyclodextrins Production and Complexing

2.1. Processes of Cyclodextrins Production and Characterization

The cyclodextrins (CD) are obtained by enzyme hydrolysis of starch in the presence of cyclodextrin-glicozil-transferaze (CGT) produced by numerous microorganisms (Bacillus macerans, Klebsiella oxytoca, Bacillus circulans, Alkalophylic bacillus, etc).

The CD preparation occurs in two phases: in a first stage, the partially pre-hydrolyzed starch is treated with the CGT enzyme, resulting in a mixture of α-, β- and γ- CD together with a series of linear dextrans (Grigoriu, 2009). In the second phase, the separation of cyclical and linear products of starch enzyme degradation occurs. The simplest method to separate the α-, β- and γ- CD from the reaction mixture is the selective precipitation by forming inclusion
complexes with an adequate guest molecule (for example, α-CD crystallizes by adding cyclo-hexane, 1-decanol; β-CD can be separated by forming a complex with fluorobenzene or toluene; γ-CD gets separated by means of anthracene, cyclohexadecanol). In the presence of glycozil- transferaze, the helical macromolecule of starch gets hydrolytically split, and the ends of the fragments generated in this way bound together by α-1,4-glycosidic bonds. Since the enzyme does not present specificity, cycles with a different number of glucose units are obtained (Fig. 1). Due to the steric hinging and preferred conformations, no cyclo-dextrins with less than 6 gluco-pyrazine groups in the cycle were obtained. α-, β- and γ-CD with 6, 7 and 8 glucose rests are obtained in the biggest amount; yet, the literature reports also CD with more than 100 glucose groups.

The CD structure presents a series of peculiarities:
− the classical “seat” conformation of the rigid remains of α-D-glycopyranose;
− specific distribution of the hydrophilic and hydrophobic groups: seen from one side, the CDs look like a truncated cone, empty at the inside (Fig. 2), being frequently described as annular macro-cycles.

The secondary OH groups are situated on the big basis, and the primary OH groups are situated on the small basis of the truncated cone. The presence of the hydroxyl groups on the both bases of the truncated cone confers the CD a good solubility in the aqueous solution. The inside of the CD cavity is
hydrophobic (it is in line with the hydrogen atoms of the CH groups, as well as with the glycoside oxygen atoms). In consequence, these cavities form a hydrophobic matrix in a hydrophilic environment, described in the specialized literature as “micro-heterogeneous surrounding” given the orientation of the hydroxyl groups: the secondary groups, directly attached on the glucopyranosic ring, are rigid, while the primary O(6)H groups can turn around the C(5)-C(6) bonds, adopting the orientation (-) or (+) gauche (Fig. 3).

The (-) gauche form, the mostly spread, has the O(6)H group directed toward the outside of the cavity.

Fig. 3 – Conformation of glucose unit with O(6)H in (-)gauche and (+) gauche orientation (Grigoriu, 2009).

The (+) gauche form, with the O(6)H group directed toward the cavity centre, can only occur when the packing requirements of the molecules from the lattice of the inclusion complex needs it or if a guest including hydrogen bond is formed.

− the form of the CD cavity is not cylindrical, but slightly truncated; the cavity diameter depends on the number of glucose units, and the micro-cycle height remains constant (Fig. 2).
− the existence of a cycle of hydrogen bonds between the O(2)H and O(3)H groups of the adjacent glucose units, which stabilize the molecule shape and significantly influences its solubility in water (Grigoriu, 2009).

Given the specific molecular structure, the main characteristic of CD is its capacity to include different guest molecules, such as: polar compounds (amines, acids, esters, etc), aliphatic and aromatic hydrocarbons, rare gases, oxygen, carbon dioxide and even polymers. As a rule, the inclusion complexes are solid crystalline substances, stable under certain temperature and pressure conditions, resulting from the spatial reunion of molecules, without affecting the system of chemical bonds of the components. They are formed by the inclusion of one “guest” (or “included”) component within the free space of the crystalline lattice of the other component, called “host” (or “support”).
2.2. Factors that Influence the Guest Controlled Inclusion and Release

The cyclodextrins are typical host molecule; they form inclusion complexes with a very wide range of guests, the main requirement being that these molecules are completely or partly accommodated inside the host molecular cavity (complementary from the stereo-electronic standpoint). As a peculiarity, the inclusion complexes of CD can exist both in solution and in solid state. In aqueous solution, the weakly polar CD cavity is occupied by the water molecules which, given the energetically unfavorable environment (polar-apolar interactions), are easily substituted by the guest molecules, less polar than the water. The driving force which leads to the generation of inclusion complexes of CD is generated by the exchange of water molecules with the hydrophobic guest molecules. Moreover, interactions appear between segments of guest and host non-polar molecules, and the cycle stress decreases, which results in a low energy steady state. The cyclodextrins are not bound with the guest molecules through strong chemical bonds. In fact, it is about the van-de-Waals forces, the hydrophobic interactions and possible hydrogen bridges. Yet, given their specific spatial distribution, they can be so strong as to reach the strength of a covalent bond. Therefore, the cyclodextrins can be easily separated through physical processes like the extraction with vapors or from solution, by preferential complexing or by ultrasounds. A thermodynamic and kinetic balance is rapidly established in solution (Fig. 4) (Gröger et al., 2001).

Normally, the molar ratio between the cyclodextrin and the guest molecule is of 1:1. Yet, with certain compounds more cyclodextrin is necessary. The system is considerably influenced by the following factors:
- cyclodextrin type;
- variations of temperature, concentration and pH;
- solvent polarity;
- the presence of other compounds.

Fig. 4 – Schematic representation of the dynamic balance at complex formation (Buschmann et al., 2001).
When the complexes are undone, the reversed process occurs. A certain water amount is necessary. Usually, the dissociation occurs quickly because, when water is added, the number of water molecules around the cage quickly increases. Despite the initial dissociation energetic barrier, given the existence of the interactions between guest and host molecules, it is the concentration gradient which prevails, and the guest molecules leave the host molecules. Given the small concentration in solution, the complex reformation is impossible and the released molecule remains in solution or precipitates.

3. Cyclodextrin Application on Textile Substrates

3.1. Adequate Functionalizing of Cyclodextrins and Application on Textile Substrates

Investigations have been made in the textiles field for cyclodextrin fixation on fibers, with the view to make use of their capacity to form inclusion products with various substances that are to be released later, substances like: fragrances, antimicrobial substances, insecticides, UV-absorbers, various medicines with trans-dermal administration, etc. The cyclodextrins linked to the textiles can also be used to collect the perspiration, in order to establish a diagnosis later. Yet, all these are only possible if the CD is fixed on textile fibers.

Nevertheless, there is also the possibility to use the CDs that are not chemically or physically fixed on the textile material. For instance, the unpleasant smells from the textiles can be removed by CD complexing. The textile product is treated by spraying it with a CD-containing solution, and after retaining the smells, the formed complex is removed by washing. In this case, the CD is no longer recuperated, being removed together with the smells. In the following, we shall direct our attention to the case when the CDs are permanently fixed on the fiber. Here there are two situations: physical fixing, through long alkyl chains or other hydrophobic groups, as is the case with polyester (Fig. 5a), where the polar part of the CD derivative remains at the polymer surface also in the case of chemical fixation through reactive groups (Fig. 5b), a case applicable for cellulose fibers and not only.

Since the CDs do not react by them with the textile material, their reactive derivatives are necessary. By parity of reason with the dyeing processes, a mono-chlorotriazinyl reactive group was grafted on the CD molecule, the result being monochlorotriazinyl- β- cyclodextrin (MCT- β-CD). This substance was produced at a mass scale and made available for chemical textile finishing starting with the year 1996 and can be applied by immersing the textile material in a bath, padding through and then washing the unfixed MCT- β-CD.

The reaction is a nucleophilic substitution of the cellulose hydroxyl groups to the chlorotriazine cycle (Fig. 6).
The fixed CD molecules can be used, for example, for catching the smells or for repeated perfume refilling. The caught fug and perspiration smell will be removed in the washing machine. The spaces inside the CD molecules can then catch new substances. On the other side, the textiles can be enriched with various scents.

Beside this, one can also apply antimicrobial substances. These will be gradually removed, through the action of humidity, for example. The higher the humidity content, the higher the amount of released substance. Therefore, the material reacts to changing conditions. As applications, we can quote the T-shirts, clothes, decorative materials, etc. (Gröger et al., 2001).

Fig. 5 – Schematic diagram of fixation of CD derivatives with hydrophobic groups (a) and with reactive groups (b) at the polymer surface (Buschmann et al., 2001).

Fig. 6 – Cyclodextrin chemical bonding to the monochlorotriazinyl group and then to the textile fibre.
Another method to fix the CD on cellulose fibers is to use hetero-
bifunctional dyes which include two types of reactive groups and possess a high
deposition capacity, uniformity and good washing resistance. The chemical
bonding of β-CD molecules to cellulose is proposed, by using these dyes,
followed by complexing, for instance with essence oils of rosemary, lavender,
jasmine or sandal wood, of the already fixed CDs which will slowly release the
retained substances (Chao-Xia & Shui-Lin, 2004). The experiment uses de-
sized and bleached cotton cloth and reactive dyes like the one in Fig. 7,
containing monochlorotriazine and vinyl-sulphonic reactive groups.

The dye liquor contains the dye, β-CD, natrium chloride as electrolyte,
ph = 7; temperature 45ºC; hydro-module = 40:1. After 30 min, the pH value is
increased at 10.5 and the temperature at 80ºC, and the dyeing is continued for 45
min. In the end, a normal washing with 2 g/L natrium carbonate and 2 g/L non-
ionic detergent is carried out for 30 min at 60ºC.

Fig. 7 – Reactive dye.

The dyeing liquor depletion is then measured with an UV-3000-Vis.
Spectrophotometer. One compares the color intensity before and after the
washing and determines the β-CD concentration on the textile material by
means of the phenol-phtalein test paper. The intensity of phenolphthalein color
is proportional with the β-CD concentration, because the phenolphthalein is able
to form an inclusion complex with β-CD. The cloth treated with at most
0.01x10^-3 mol/L β-CD is introduced in water with a known phenolphthalein
content (smaller than 0.35x10^-3 mol/L) at pH= 10.5. Then the concentration is
evaluated at the maximum absorption wavelength (553 nm). The vessel is
agitated at the room temperature to permit the phenolphthalein inclusion in β-
CD. The cyclodextrin concentration on the cloth is calculated as the difference
between the absorbance degree before and after inclusion.

In conclusion, the β-CD fixation on the cloth depends on the dye
reaction with cyclodextrin and the fiber. The dye and β-CD concentrations
influence the amount of CD fixed on the fiber, while the dye structure
influences its reactivity with both β-CD and cellulose. The cellulose and β-CD
hydroxyl groups present a similar reactivity. A β-CD molecule can be fixed on
the fiber only if one of the dye reactive groups is able to react with one of its
hydroxyl group, and the other reactive group with a cellulose hydroxyl group.
In this way, the dye molecule acts like a bridge, as one can see below:
Cellulose- O- Dye- β-CD

An alternative is that the β-CD molecule is attached to two dye molecules, making up a longer bridge:

Cellulose- O- Dye- O- β-CD- O- Dye- O- Cellulose

At the same time, the active chlorine from the triazine cycle can react with each of the two hydroxyl groups (one from β-CD and the other from cellulose). The bi-functional dyes show different reactivity with respect to cellulose and β-CD respectively, due to different structure of chromophores and bridge-groups. The experience shows that, as expected, an increase of the initial β-CD concentration leads to an increase of its amount on the cloth, but only up to a certain limit.

3.2. Cyclodextrin Application on Other Textile Supports

Attaching the cyclodextrins to synthetic textile fibers (polyester, polyamide, etc) presents the same interest as attaching them to natural fibers, given the fact that, as has been specified before, they present the advantage to incorporate other molecules, a property which is implicitly transferred to the textile material and can confer it new properties. In the case of polyamide fibers (PA) used in the medical field for different prostheses, such as artificial ligaments, tendons, inguinal meshes, etc, one can avoid the infections especially hazardous for patients either by using silver containing implants, or by locally administrating the antibiotics. A systematic antibiotic administration presents the shortcoming that only a small part of the administrated medicine reaches its target. For local administration, one can immerse the implant into an antibiotic solution before utilization. Yet, many biomaterials show a poor affinity for antibiotics and they are released during a too short a time to be useful for the patient. That is why an improvement of antibiotic sorption and release is proposed, by modifying the biomaterial surface, namely by making it functional with CD.

The cyclodextrins are attached to the PA fibers by means of the citric acid (CTR) as reticulating agent. Yet, as one can notice from Fig. 8, the reaction occurs between CD and CTR, while PA is not involved and therefore the reticulating agent makes no covalent bonds with the fiber. When the two reactants are used simultaneously, only the CD and CTR poly-esterification occurs, a polymer named poly-CTR-CD resulting. This interacts with the fiber, forming a hot water resistant continuous film. By finishing with CD, the textile substrate becomes a good biomaterial candidate. The test of drop angle has proved that the fibers wettability increases and the biological studies indicated both a very good compatibility of the CD grafted with the textile, and the non-toxicity of CD and cyclodextrin polymers. If one uses the PA functionalized with hydroxypropyl-γ-CD (HP- γ-CD), a proliferation and an increased vitality of the cells next to the biomaterial cells are obtained. The good adhesion kinetics observed at the polyamide grafted with HP- γ-CD could be explained by the increasing
wettability of the treated cloth. The UV spectrometry reveals a 10 times increase of the absorption in the grafted HP-γ-CD cage molecules, as compared to the virgin PA, which permits the inclusion of large amounts of antibiotics, and therefore a stronger and lasting antimicrobial effect (Ghoul et al., 2008).

By using the β-cyclodextrins and the butane-tetracarboxyl acid (BTCA) as reticulation agent which acts (by the impregnation of polyester and reticular textile at 150ºC) to increase the cyclodextrin durability on the textile material, one can obtained spaced polyester textiles with improved properties, due to the insertion of hydrophilic groups and hydrophobic voids. An increase of dyeing capacity can be obtained if the reactive dyes are used and, as absorbing product, the polyester becomes able to absorb chromium ions (Montazer & Jolaei, 2010).

Fig. 8 – Cyclodextrins reaction with citric acid (Ghoul et al., 2008).

Fig. 9 – β-cyclodextrins reticulation with butane-tetracarboxyl acid (Montazer & Jolaei, 2010).
4. Utilization of Cyclodextrins Grafted on Textile Substrates in Medical Purposes

4.1. Gradual Release of Medicines

The cyclodextrins facilitate the biological membranes penetration. Due to their big size and the hydrophilic outside, they are not able to penetrate the membranes by themselves. Yet they play the role of carrier, leading the complex medicine molecule in solution near the lipophyl membrane, where, without being hydrated, this molecule penetrates directly the membrane (Fig. 10).

![Visualization of the function of facilitation of biological membrane penetration](image)

The interaction of the β-cyclodextrins with *Salvia sclarea* essence oil has been investigated by the Chinese scientists (Tian et al., 2008) by spectral fluorometry and various factors that affect the inclusion process were examined. At the same time, the formation constants at different temperatures were determined and the thermodynamic parameters (H, S, G) were calculated. The molecular microcapsule of *Salvia sclarea* essence oil was prepared by the method of saturated aqueous solution and the microcapsule stability was determined. The result suggests that: the stoichiometric ratio (molecular ratio) between the CD and the essence oil is 1:1; there is a diminution of the formation constant with increasing temperature; the order of availability of association with the *Salvia sclarea* essence oil is: \[\beta-CD > 2,6\text{-dimethyl-} \beta-CD > \text{mono}[2-O-(2\text{-hydroxyethyl})]- \beta-CD > \text{mono}[2-O-(2\text{-hydroxypropyl})]- \beta-CD.\]

The thermodynamic measurements indicate that the inclusion process is exothermal, enthalpy controlled and accompanied by a negative entropy contribution. The van-der-Waals forces play an important role in the process.

The vascular grafts made of woven polyester are used for replacing or by-passing the deteriorated artery. In order to minimize the infection hazard during and after surgery, the polyester prostheses were functionalized with cyclodextrin polymers in order to obtain a controlled release of antibiotics.
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(cyprofloxacine, vamomicin and rifampicin). The epithelial cells were used to determine the antibiotics viability, while the human micro-vascular endothelial pulmonary cells were used for cell proliferation (by counting and by utilization of the method with fluorescent Almar blue dye for vitality).

*Staphylococcus aureus, Escherichia coli and Enterococcus sp.* were used to determine the anti-microbial activity. When comparing the prosthesis of polymer grafted with cyclodextrin containing antibiotic, and the antibiotic applied as such on the prosthesis, it was found out that the antibiotic incorporated in cyclodextrin is absorbed to a greater extent and presents an increased antimicrobial activity. The viability test indicated the rifampicin and cyclofloxacine toxicity and the absence of vancomicine toxicity. This test permitted to explain the poor viability and proliferation of the human micro-vascular endothelial pulmonary cells in the case when the prostheses coated with polycyclodextrin containing antibiotic was used. This is not produced by the functionalization process, but by the cyclo-toxicity of the antibiotic in itself. This kind of property can be exploited in order to fight the intracellular bacteria, such as tuberculosis and other diseases, without compromising the *in vivo* applications of the functionalized prostheses (Blanchemain *et al.*, 2008).

For inflammation treatment, the intelligent textiles offer favorable solutions that remove some of the inconveniences of the traditional treatments, such as: sensitivity of certain patients to the medicine administration by mouth, omission in the case when the children and old people forget, a too frequent change of bandages in the case of the common bandages. A bandage able to gradually release the necessary medicine at the inflamed place avoids the above mentioned difficulties. The structure of such a bandage consists in an absorbing matrix, such as a cotton cloth, which contains an anti-inflammatory medicine (sodium diclophenac, for example) included in the cyclodextrine linked to the textile material by means of a reticulating agent, like dimethyl-di-hydroxyl-ethylene urea (DMDHEU). The bandage is executed in two stages: medicine complexing with cyclodextrin, followed by attaching the complex to cotton using the reticulation agent (Fig. 11).

If the textile is impregnated in a vat containing ethanol, the rate of medicine release increases at the beginning, when the inflammation is severe. If the bandage is not treated with ethanol, the initial release of medicine is slow. At the same time, the increase of the medicine release rate is not proportional to the initial concentration (Montazer & Mehr, 2010).

### 4.2. Characterization of the Cyclodextrin Biological Activity

In view of rational utilization of cyclodextrin to make functional the textiles with medical destination, namely for dermal administration of medicines and for other topic formulas, in the year 2006 researches were carried out financed by the Federal Ministry of Education and Research from Germany.
These researches suggest the therapeutic value of cyclodextrin in inducing the apopthesis in the case of skin cancer.

The research purpose was to investigate the influence of various cyclodextrins on the cell proliferation by using HaCaT keratinocites in the *in vitro* testing system. Moreover, the study was carried out in order to establish the harmless concentrations in the case of dermal applications. Using different *in vitro* tests, it has been established that the α, β and γ- cyclodextrins in concentrations of up to 0.1% have no anti-proliferating influence on the HaCaT-keratinocites. Sometimes, there are proliferating effects, but, except for γ-cyclodextrins and their derivatives, the utilized cyclodextrins, in concentrations of 0.5 and 1.0% respectively, exert a citotoxic influence on the HaCaT-keratinocites proliferation. On this basis, the following sequence was proposed in terms of citotoxicity (Hipler *et al.*, 2006): methyl- β-CD > β-CD> hydroxypropyl- β-CD > α-CD > (γ-CD).

The requirements imposed to the textiles used near the skin in medical purpose are:

- no skin irritations and no negative impact on the environment;
- extremely restricted chemical interactions with other ingredients from the textile material;
- favorable chemical interactions;
- deposit the medicines which cure or create comfort;
- release the curing substances;
– create benefits for the sensitive skin (as in the case of patients suffering from atopic dermatitis) and moisture retention;
– complex the stinks;
– collect the perspiration components (with diagnosis purposes);
– collect/inhibit the function of releasing the skin irritant substances, thus supporting the skin immune system;
– diminish the accumulation of unwanted substances deriving from perspiration, which can cause skin discomfort (Knittel et al., 2002).

4.3. 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 β-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 (Buschmann et al., 2001).

5. Other Applications of Cyclodextrins

The cyclodextrins play a significant role in the textile industry, as they can be used to: remove the surfactants from the washed textile material; replace the surfactants in wet processes; textile finishing; bonding the chemicals on the fibers in order to increase the wettability, include fragrances, remove the insects, antimicrobial action, etc.

The cyclodextrins can be considered as a new class of auxiliary substances for the textile industry. It is very important that the amount of oxygen necessary for waste water treatment is diminished if the cyclodextrins are used
instead of usual chemicals in the textile finishing processes. They can also act as anti-foaming agents, thus reducing the water consumption during rinsing.

By treating the acryl fibers with cyclodextrin (or with a cyclodextrins oligo-polymer), an insecticide and a siloxan, one can obtain an insecticide effect that resists to more than 20 washings. As insecticide, one can use the isobornylthiocyanacetate (Szejtli, 2003). It can be applied to the cellulose fibers either by traditional impregnation, or by covering with an insecticide against anopheles, named limonene. For the traditional method, the monochlorotriazinyl- β-cyclodextrins and a polymer binder are used, with good washing and storage results (Hebeish et al., 2008).

Still another important cyclodextrin application consists in the antimicrobial treatment of hospital bed clothes; one can use cyclodextrin inclusion products with antimicrobial organic volatile agents, active against Candida albicans and Staphilococcus aureus.

In the field of textile dyeing, the cyclodextrins (polymerized, by 2-5 units) offer solutions for the application of dyes at warp sizing, while during desizing, given the water solubility, the cyclodextrins are removed, and the dyes, especially the reactive ones, remain on the fiber (Szejtli, 2003). The successful utilization of the solid complexes of the soluble (direct, reactive, acid) and insoluble (dispersion, for ex.) dyes with cyclodextrins, for dyeing certain fibers presents the advantage that no other supplementary auxiliary compounds are necessary in the dye liquor. The utilization of cyclodextrin complexes with dispersion dyes for polyester high temperature dyeing results in a higher degree of bath depletion, while in the standard dyeing process with accelerators a big amount of dye remains unfixed in the dye liquor (Grigoriu, 2009).

The treatment of waters containing a large amount of heavy metals (bivalent cations of lead, cadmium, zinc and nickel) becomes possible by using unwoven polyester materials sized with co-polymers of β-cyclodextrins and different polycarboxyl acids (citric acid, butane-tetracarboxyl acid, polyacryl acid). A textile material is obtained with cation exchange properties due to the carboxyl groups which did not reacted with cyclodextrin. The presence of cyclodextrin which possesses those hydrophobic cages, offers the possibility to include aromatic molecules or other organic pollutants (Ducoroy et al., 2008).

6. Conclusions

Taking into account the multitude of cyclodextrins applications in the textile area, already accomplished during a relatively short time (since 1990, when the first patent concerning their utilization in textile field was registered), one can suppose that in the near future new areas of application will emerge, both in the chemical textile technology and in the area of smart textile products, such as in medicine. The permanent fixation of the functionalized industrial cyclodextrins on textiles, as well as their capacity to form inclusion complexes
with various substances offer unrestricted possibilities. The accomplishment of investigations concerning the kinetics of guest-substances releasing from cyclodextrin cavities, and the study of the factors that influence this phenomenon appear as a necessity of the future evolution in the utilization of these substances, especially in medical area.

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REFERENCES


NOI APLICAŢII ALE CICLODEXTRINELOR ÎN TEXTILE

(Rezumat)

Este cunoscută de mult timp capacitatea ciclodextrinelor de a forma compleşii de incluziune, proprietate utilizată în domeniul textil pentru obţinerea unor produse cu aplicaţii în creşterea confortului la purtare, cât şi pentru realizarea textiilor medicale. Sunt posibile însă mereu noi aplicaţii ale acestor compleşii, fie prin fixarea permanentă pe textile, fie în ecologizarea şi creşterea performanţelor unor procese din industria textilă sau din domeniul epurării apelor uzate.

În direcţia creşterii confortului la purtare, ciclodextrinele serveşc la îmbunătăţirea hidrofiliei şi la antistatizare, pentru captarea mirosurilor şi a transpiraţiei sau la eliberarea pentru un timp îndelungat a parfumurilor incapsulate în prealabil.

În domeniul medical, cu scopul de a obţine o eliberare lentă de antibiotice şi pe baza capacitaţii ciclodextrinelor de a forma reversibil compleşii de incluziune cu acestea, s-au creat proteze vasculare funcţionalizate care să reducă riscul infecţiilor postoperatorii. Pe acelaşi principiu, s-au realizat tratamente transdermale cum ar fi obţinerea unui pansament capabil să elibereze diclofenac de sodiu, ca medicament antiinflamator. Ciclodextrinele se utilizează şi pentru eliberarea substanţelor dezinfecţante sau cicatrizante la locul aplicării bandajelor pentru vindecarea diferitelor leziuni cât şi pentru realizarea de materiale textile cu activitate antimicrobiană, rezistentă şi după un număr de spălări.

În domeniul optimizării tehnologiilor chimice textile, ciclodextrinele sunt utilizate pentru îndepărtarea de pe material sau inactivarea în fază lichidă a surfactanţilor, pentru intensificarea proceselor enzimatiche sau ca egalizatori la vopsirea cu coloranţi reactivi.