Physical Modification of Cotton Surface by β-Cyclodextrin and Its Derivative*

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The research covers investigation on physical modification of pure cotton fabric using β-CD and its derivative i.e. randomly methylated β-CD (MCD). The obtained material was investigated by means of properties changes when compared to native cotton. The research on retention of small organic molecules and water was done as well. According to obtained results it might be stated that physical modification allow to avoid toxic reagents needed for chemical modification and the material possess interesting retention properties. However the application of obtained fabrics are limited to the single-use application due to washing out of carbohydrate from the cotton matrix.

Keywords: Cyclodextrins; Physical modification of fabrics; Supramolecules

I. INTRODUCTION

Cyclodextrins (CDs) belongs to the class of cyclic oligosaccharides consisting of α-1,4-glycosidically linked D-glucose units. 6, 7, and 8 membered rings are commonly known as α-, β-, and γ-CDs, respectively. By means of the molecular geometry CDs may be described as truncated cones with hydrophobic cavities that are able to bind small molecules through host-guest interactions. As a result inclusion complexes may be obtained [1–3]. Such complexes are known to play an important role in food industry, pharmaceutics, cosmetology and many other fields [3]. Its applicability is the consequence of nanoencapsulation phenomena. By complexation the small molecules of guests may be protected against heat, light or oxidation. The decrease of volatility is also an important factor on many fields (aroma-like compounds in food or cosmetics). Inclusion complexes are also a convenient tool for masking an undesirable taste or smell of medicines. The textile industry employs the cyclodextrins as well [4]. When CDs are bound to the fabric the new functional material may be obtained with plenty of possible commercial application. The complexation of some active substances allows obtaining new functional fabrics with some therapeutic or medicinal functionality. On the other hand the encapsulation of sweat molecules may also be the important property of modified material. In textiles, cyclodextrins are also known as a relatively new class of dyeing and finishing auxiliaries capable of influencing both the processing of the textile materials and their serviceability properties [5–7]. There is plenty of ways to link the CD and a fabric together. Most of them include chemical bonding using toxic or non-friendly chemicals. The most common way to covalently bond the CD with fabric is the premodification of CD molecules using monochlorotriazinyl-β-cyclodextrin (MCT), t-butyldimethylsilyl (TBDM) derivatives, 6-A-O-p-toluenesulfonyl-β-cyclodextrin (TS), N-methylacrylamide, policarboxylic acids and many others [8–15]. The main problem with chemical modification of CD is the yield of the reaction and selectivity. In most cases the randomly modified CD mixture is obtained. The phenomena impede the further fabrics modification.

According to that we have investigated the physical modification of textiles using β-CD and permethylated β-CD as a greener alternative to complicated and chemicals employing methods.

II. EXPERIMENTAL

For investigation of physical fabrics modification four different cellulolic fabrics were investigated and designated as follows: T – single weave cotton, 2T – double weave cotton, F – flannel fabric, C – “Camel fabric”, a commercial fabric employing as an inner part in shoes producing processes. For modification CAVASOL® W7 M i.e. randomly methylated β-cyclodextrin (MCD) and β-CD (Roquette, France) were used. All other chemicals were purchased from POCh, Poland and were analytical
grade and used as received.

A. Physical modification of fabrics

The modification was done by soaking the fabric in the MCD or β-CD solution that varies in concentration. The process was done in alkali solution (sodium carbonate solution) in order to additionally clean the surface of the fiber. In a typical experiment using MCD approximately 10 g (62 mmol of anhydroglucose cellulose’s units) of fabric was put into the Erlenmeyer flask. To the fabric an aqueous solution of sodium carbonate Na₂CO₃ was added (20 g Na₂CO₃ in 250 mL of distilled water). After the fabric was fully soaked by the solution MCD was added (20 g, 15 mmol). The flask was then closed and the content was thermostated at 95°C ± 5°C when shaking. After 1 hour the fabric was taken and washed three times in distilled water and left dry at ambient temperature.

In typical β-CD experiment approximately 10 g of fabric was soaked in β-CD solution with different concentration. Due to partial insolubility of β-CD in water for higher concentration the binary solvent composed from water and 2-propanol were used. The detailed information on soaking solution is presented in Table I. Fabrics were soaked in solution at 100°C (±5°C) for 1 hour as it was described for MCD modification. After 1 hour the fabric was taken out, washed three times in distilled water and left dry at ambient temperature. For complexation eugenol (4-allyl-2-methoxyphenol) was chosen due to its wide use in perfumeries, flavorings, essential oils and in medicine as a local antiseptic and anesthetic [16]. Each experiment was done in triplicate.

| β-CD concentration | solvent                |
|---------------------|------------------------|
| 0.37                | water                  |
| 1.45                | water                  |
| 5.35                | Water/2-propanol - 75:25 (w/w) |
| 8.78                | Water/2-propanol - 75:25 (w/w) |

D. Liquid phase sorption

The sample preparation involves the fabric sample (1 g±0.1 mg) hanging over the alcoholic solution of eugenol (50 mL, 10 mmol/L). The fabric sample was put into the solution and mercerized for about 15 min. After the sorption was finished the sample was taken off the solution, squeezed and left dry in ambient temperature. The dried sample was put into the 20 mL of 1M NaOH and shake for about 1 min. The exact 1mL of the extract was neutralized by 1mL of 1M HCl. To the sample 500 μL of Follin-Ciocalteu reagent and 10mL of 1M Na₂CO₃ were added. The sample was left to equilibrate for 1 hour and then the absorbance at 750nm was measured against blind sample (1mL 1M NaOH, 1mL 1M HCL, 500 μL of Follin-Ciocalteu and 10 mL of 1M Na₂CO₃). The amount of eugenol was calculated according to calibration curve based on known concentration of eugenol.

E. Gas phase sorption

The complexation ability of fabric was tested as a function of time, so the amount of eugenol was analyzed after 1, 3, 5 and 7 days of experiment. The sample preparation involves the fabric sample (1 g±0.1 mg) hanging over the alcoholic solution of eugenol (5 mL). The experiment was conducted at 22°C in the constant humidity. The samples of fabric were hanged in order not to touch each other during the complexation. The blind sample (unmodified fabric) was put into the experiment as well. After the specific period of time the sample was taken of and put into the flask. To the flask 20 mL of 1 M sodium hydroxide was inserted. After 1 minute of shaking the fabrics was thrown away and the extract was analyzed as for liquid phase experiments.

III. RESULTS AND DISCUSSION

As a result of investigation a series of modified fabrics were obtained. The introducing of MCD and β-CD onto fabric’s surface was done at higher pH (alkaline condition) in order to pre-clean the surface of the cellulosic fiber. The aperture on the fiber that is sometimes hydrophobic from nature may inhibit arising of physical forces between CD and the fiber. In case of physical modification, when the CD-fiber interrelationship is concerned the only two
mechanisms may be in focus (Figs. 1 and 2). In first one “the cones” of CD are filled up with cellulosic chain. The described mechanism will result in one main CDs properties change. The ability to form the inclusion complexes will be blocked due to occupation of internal space by the polysaccharide chain. So the fabric will be modified but no CDs complexation ability will be observed. It is also worth to point out that the inner part of CDs ring is rather hydrophobic and anhydroglucose units of cellulose are hydrophilic. The string of one type of molecule on the second one will not be the preferable interaction but cannot be omitted. The mechanism proposed on Fig. 2 shows CD/AGU (Anhydroglucose Unit) interaction as the result of AGU units presented in both compounds. Each AGU possess three hydroxyl groups (primary at C$_6$, and secondary at C$_2$ and C$_3$ respectively). High electronegativity of oxygen atom causes the hydrogen bond to be present in all carbohydrate based systems. It might be the intra—or inter-molecular bonds. The proposed mechanism will not block the cavity for complexation and allow the CD to be even partially bond to the fiber. The situation will change in case of oil based synthetic fabrics that are rather hydrophobic. In that case the stringing will be the preferred mechanism and the structure of rotaxane or pseudorotaxanes will be obtained. In fact rotaxanes will not be able to complex any small molecules. In fact, in case of cellulose both mechanisms may be observed simultaneously. Due to the fact of weak CD/fiber interaction it must be said that investigated modification may be useful only in case of disposable application unless the re-modification will be done once the material was used. Going into detailed results of investigation discussed below it may be stated that obtained substitution is sufficient for treating the material as functional. Additionally, in all cases the amount of CDs at the fabrics does not depend on type of the fabric or even on entanglement closeness. In general the amount of more hydrophilic β-CD is higher in the obtained material when compared to MCD. The differences will lie in polarity of side groups i.e. hydroxyl group in β-CD and alkoxyl group in MCD. The obtained result may testify that hydrogen bond mechanism takes places during the modification course. For β-CDs the amount of cyclodextrin at the surface is a quadratic function of CD concentration in a soaking bath. As it is known the ability to form host-guest complexes is strictly guest size, shape and properties dependent. So the complexation ability may be compared only if model guest is used. The known methods of sorption investigation by CDs modified fabrics may be divided into two groups. First bases on organoleptic classification of flavor compound retained at the fabric [14]. In the second group the concentration of

| Fabric | ∆m (g) | Mass increment (%) |
|--------|--------|--------------------|
| T      | 0.03   | 0.27               |
| 2T     | 0.01   | 0.08               |
| F      | 0.02   | 0.20               |
| C      | 0.04   | 0.39               |

| Concentration of CD in soaking bath [% (w/w)] | ∆m (g) | Mass increment (%) |
|-----------------------------------------------|--------|--------------------|
| F                                             | 0.02   | 0.02               |
| 2T                                           | 0.04   | 0.04               |
| F                                             | 0.12   | 0.12               |
| 2T                                           | 0.12   | 11.51              |
| F                                             | 0.23   | 0.25               |
| 2T                                           | 0.25   | 24.03              |

FIG. 2: Hydrogen bond based mechanism.

FIG. 3: Degree of modification for MCD processes.
guest molecule retained in the solution is measured using instrumental analysis [17]. Following the second method we used the method known for identification of phenol like compounds with Follin-Ciocalteu reagent [18, 19]. In our case the eugenol complexation was performed. Investigation was done according to gas and liquid phase adsorption. The research covers the β-CD modified material because MCD gave relatively small degree of modification. For detailed investigation two fabrics was chosen: T and F. For those fabrics a modification was done as described in experimental section. As the result a series of new materials was obtained.

In the both series the amount of CD at the fabrics surface varied between 15 to 250 mg/g of the fabric. The differences in eugenol sorption as a function of CD concentration were shown for two fabrics in Figs. 6 and 7, respectively. In all case two method of desorption differing in desorption temperature (ambient and ≥85°C) were used. Obtained results allow to state that the highest eugenol content was observed when the CD concentration reaches about 40 mg/g. The phenomenon is easy to observe in case of 2T fabric when compared to 20 and 120 mg/g. The increase of sorption is about 60% (w/w). The increase in CD content results in decrease of eugenol sorption. It may be explained in fact that higher CD molecules concentration causes the agglomerate to create. In such kind of macrostructure the inner of CDs cones is screened by other molecules of an aggregate. Such kind of phenomena has already been observed in earlier work [20].

The amount of eugenol at the fiber seems to be extraction method independent. It may testify that eugenol included in CDs cavities will not evaporate even at higher temperature. The phenomenon may be also proved when sensory analysis is done. Sensory panel did not recognize the eugenol smell after heating the sample. It means that evaporation of eugenol physically adsorbed at the fiber took place. The phenol complexed by CD remains in the cavities.

The results obtained for gas phase encapsulation differ dramatically to those discussed before. The results of gas phase experiments are presented in Figs. 8 and 9. For both investigated fabrics the overall eugenol content increase. It testifies that the wave of the fabric does not influence on sorption. On the other hand the differences between blind sample and modified fabrics cannot
be omitted when the sorption takes more than 24 h. In general the amount of adsorbed eugenol will increase in time in both cases but the dynamics of the process will differ completely. What curious, the sorption of eugenol on blind sample i.e. unmodified fabric is much higher to those observed after CDs modification. In case of 2T fabric the concentration of eugenol after 7 days of experiment is about four times lower in modified fabric than for blind sample. The explanation of phenomenon may lie in pore diameters changes in fabric. The wide pores in blind sample allow eugenol to penetrate them freely. The surface of this sample is more expanded and physical interaction cellulose—eugenol takes place. It results in higher eugenol adsorption. Modification of fabric causes diminishing of the pore size according to cellulose shrinkage in alkali condition and filling the pores by CDs. The final result is smaller diameter of the pore that is difficult to penetrate by the eugenol (see Fig. 10).

Additional investigation was done by scanning electron microscopy of the fabrics surface. It allows observing the changes in surface topography by modification. As it easy to see according to different fabrics the different topography of the wave will be observed (Fig. 11). Comparing those pictures to SEM obtained for mod-

FIG. 8: Sorption of eugenol from gas phase at modified F fabric. A – blind sample; B – modified fabric.

FIG. 9: Sorption of eugenol from gas phase at modified 2T fabric. A – blind sample; B – modified fabric.

FIG. 10: Pores at the fabric surface: A – modified fabric; B–blind sample (1 – surface of the fiber, 2 – pores, 3 – surface of the pore that is available for eugenol sorption).

FIG. 11: SEM microphotographs of fabrics. Magnification 4.5 × 10³. Designation: (A) 2T; (B) F.
FIG. 12: SEM microphotographs of modified fabrics. Magnification $10 \times 10^{3}$; CD concentration in solution $-8.78\%$; designation: (A) 2T $- CD$; (B) F.

Modified fabrics (Fig. 12) one can see the presence of light substances in form of aggregates. Due to preparation method those aggregates may be designated as CDs. The obtained pictures confirmed the information on CDs aggregation tendency [20]. Obtained pictures show that CD arrangement on the fiber is fully stochastic. It should be the result of fiber entanglement and accessibility of the fiber for cyclodextrins molecules diffusion.

IV. CONCLUSION

As a conclusion it is worth to point out that the ability to form a physical bonding between $\beta$-CD and MCD with cellulosic fiber was confirmed. According to above it may be stated that physical linking takes place as inclusion complex of CDs and small fiber particles or the hydrogen bonding between CDs hydroxyl and AGU hydroxyls. First mechanism blocks the CDs cavity for further complexation. On the other hand the amount of CD at the fabrics surface depends on carbohydrate concentration in the solution but is fiber type independent. Modified textiles possess the ability to form host-guest inclusion complexes, so they may be used for functional material preparation however it is restricted for disposable application only. The sorption of small molecules is possible from gas or liquid phase but the physical CD independent sorption mechanism cannot be omitted. On the other hand the procedure of modification looks easy and cheap what may favor the investigated method when compare to chemical or biochemical modification.

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