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Processes of Cyclodextrins grafting on cotton

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ABSTRACT

Some preliminary studies on chemical modification of cotton(cellulose) by cyclodextrins are presented. As a chemical linking agent a citric acid was applied. The reaction of cyclodextrin attaching to cellulosic fibre was controlled by means of weight of the samples as well as a new spectroscopic method. Obtained results may proof the esterification reaction of cellulose repeating unit in the presence of β-cyclodextrin and hydrogenposhate alkali salt as catalyst.

KEYWORDS

cyclodextrin, cotton, cellulose, esterification, functional fiber

INTRODUCTION

Cyclodextrins (CD) are well known as macrocyclic oligo-saccharides forming a broad range of inclusion complexes [1]. Such inclusion phenomena are promising in lots of application. Some of them has already find interesting industrial application in food, cosmetics and pharmacy [2]. The mechanism of complexation may be explained as the host-guest interaction. The CD's play the role of the host molecule possesing the hydrophobic gap able to bind a small, guest molecule. The complexation of gast molecule influences strongly on its properties including: solubility, thermal resistance, volatility or fluorescence, phosphorescence and light absorbance [3].

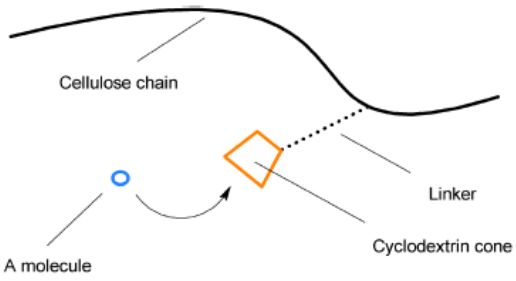

Figure 1: Cyclodextrin covalently bounded to the cellulose backbone.

One of the proposed field of employing of CD's complexes is producing functional fabrics which may carry the fragrances or in opposite are able to absorb odours (tobacco smoke, sweat etc.). Some work has already been done on this field and has been exploin by industry [4]. The main problem in binding the cyclodextrin moiety (Figure 1) with the fiber lies in finding the apriopriate linker that will selectively join together these two kinds of carbohydrates. Up to know only several methods are used from which the most popular base on sodium salt of 2,6-dichloro-4-hydroxy-1,3,5-triazole (MCT) linker i.e the triazine derivative [5]. The set up as well as th economical, ecological and health effects pushed us to investigate different methods of synthesis of these very important and promissing cellulose derivatives.

In the presented works we would like to show some preliminary studies on chemical modification of different fabrics by cyclodextrins. As a chemical linking agent a citric acid (CTR) was applied (according to the Figure 2) [6]. The reaction of cyclodextrin attaching to cellulosic fibre was controlled by means of weight of the samples. Obtained results may prove the esterification reaction of cellulose repeating unit in the presence of β-cyclodextrin and hydrogenposhate alkali salt as catalyst.

EXPERIMENTAL

Reaction setup
All investigation were performed on cotton fabrics produced by *Jomar* (Poland). The fabric was divided into samples (10 x 10cm), dried (1h. 100°C) and carrefuly weighted. Samples were than impregnated in bath containing CD (0.1% (w/v)), CTR (0.1%(w/v)) and Na_2HPO_4 - catalyst (0.06% (w/v)). After the impregnation was finished the samples were wring out and put into the hot drier for 5min (temperature of the drier was set up at 180°C) in order to run the esterification reaction according to Figure 2. Afterwards the samples were flushed by distilled water in 1 h and finaly dried at 100°C and weighted. For some samples impregantion was carried out severeal times (2 to 4) at the same conditions The blind sample was impreganted in bath containing CTR and Na_2HPO_4 but no CD.

GC-FID analysis
In order to compare the results obtained by means of weight analysis the absorption of volatile organic compounds (i.e. α-pinen) was carried out. The samples of both modified and unmodified fabrics were placed in the chamber containing 1g of α-pinene. After 7 days, the samples were thrown away from the chamber and extracted with acetone. The concentration of α-pinene in solution was measured by means of GC-FID (*Agilent*; column HP-1: 25m x 0,2mm x 0,33 µm; temperature of injector 180-250°C; injection splitless; flows: He = 1mL/min; Air = 400mL/min; H_2 = 30mL/min.

UV-VIS Analysis
UV-VIS analysis allowed to determine the amount of CD which is able to form host-guest complex with methyl orange. All experiments were done using *Helios* (USA) spectrophotometer. Sample for measurement were preppared as follows: aproximately 0.1g of fabric sample was placed in 5mL of methyl orange solution (0.03 g/L of 0.1M HCl). After 10min the absorbance of aliquot was measured at at 508nm wavelenght. The quantitative measurement were performed aided by standarisation with the solution of well known concentration of CD and methyl orange.

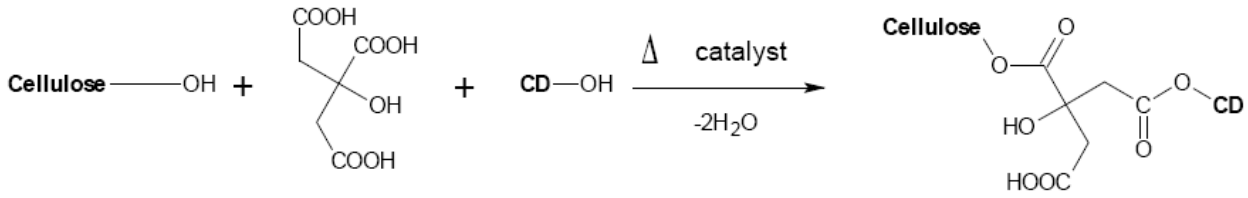

Figure 2: Esterification of cellulose and CD by CTR.

RESULTS AND DISCUSION

As a outcome of investigation we would like to state that a series of novel cellulose derivatives containing CD's were obtained. As it is easy to find out based on tabel 1 the increase in the number of reaction cycles follows the higher amount of CD binded to the fabric. The increase in the samples weight shows that the reaction of cellulose with citric acid accurs independently on CD presence in the system. If the esterification mechanism will be proofed it might be said that also the cross-linking of cellulose may occur because the citric acid posses three carboxyl able to bind hydroxyl groups of anhydroglucose repeated units of biopolymer. If the CD's are present in the system the instant increment in sample weight may be detected. The explanation of the phenomenon at early stages of investigation may be as follows:

- esterification of cellulose and CD's using citric acid as a linker;
- physical absorption of CD's at the surface of the fiber;
- polycondensation reaction of CD's and citric acid resulted in CD's polymer interpenetrated cellulosic fibers.

Due to high number of hydroxyl groups presented in the system that origin may be both cellulose and CD, all proposed mechanism may occurs at different participation levels. The phenomeno needs further and detailed explanation
All these preliminary results suggest that CD moiety is incorporated into the cellulosic matrix. The mechanism of the reaction probably involwed the esterification aided by cytric acid. The second stage of investigation allows us to state if the macrocyclic carbohydrate cones linked with the cellulose are able to make complexes with lowmolecular organic molecules. First experiments on these field has confused the team beacause as it shown at Figure 3 the number of reaction steps does not guide to the higher accessibility of the CD's cone for complexation of vapours of pinen. In order to better understanding of such phenomenon a quite new analytical method was developed. The method bases on differences in spectra of dye solution with and without CD at various concentrations levels.

Table 1. The increment of the mass of the sample after modification at various condition.

ID	Number of Cycles	Δm_{imp} [%]
K1/1	1 (blind)	8.3
K0/0	non-modified cotton	0
K1CD1/1	1	21,9
K1CD1/2	2	14,0
K1CD1/3	3	28,4
K1CD1/4	4	40,7
K1/2	2	6,6
K1/3	3	17,5
K1/4	4	16,2

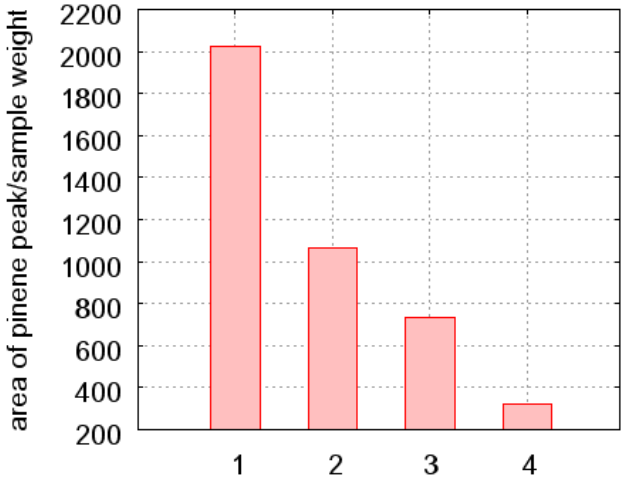

Figure 3: GC-FID investigation of vapours of pinen absorbed by the modified cellulose: 1-reaction without CD; 2- non-modified cotton; 3- one-stage modification; 4- four stages modification;

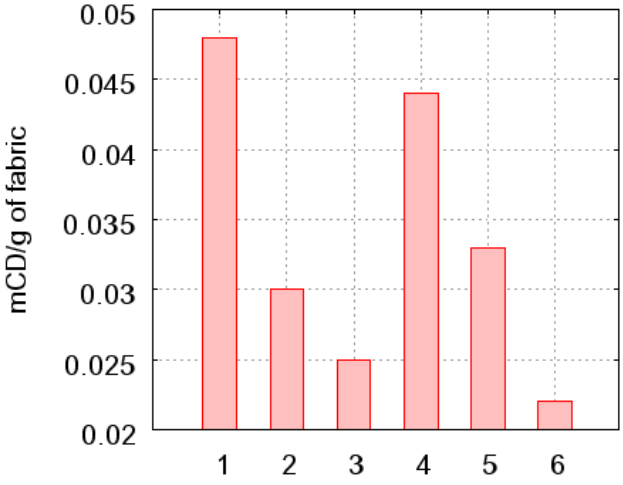

Figure 4: Spectroscopic investigation of the complex ability of modified cellulose: 1-one-stage modification; 2- two-stage modification; 3- four-stage modification; 4-one-stage modification without CD; 5-two-stage modification without CD; 6-four-stage modification without CD

As it was said the new portion of the CD's may be bounded to the fiber core -OH ar to the the CD' hydroxyl already bounded to the fiber as well. All this phenomenon guide to the high and complicated level of the organisation what influence on the materuial properties.
The experiments on host-guest complexation of bounded CD's shows that the complexation ability is the function of the number of reaction cycles and falls when the number of stages increase. The explanation of it lies in "corking" of the molecular cone of CD by citric acid (Figure 4) covalently bounded to the two primary hydroxyls of CD ring.
As a conclusion it is worth to pointed out that simple set up, cheap reagents and relatively gentle conditions of described method might be very useful for

producing special fabrics for different targets and are very promising, however a detailed investigation of the mechanism of the reaction as well as quantity analysis and the physicochemical properties of a new cyclodextrin containing material needs further investigation and are going to be the very next step of the research.

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