

SURFACE MODIFICATION OF SYNTHETIC AND NATURAL FIBRES BY FIXATION OF CYCLODEXTRIN DERIVATIVES

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ABSTRACT

It is demonstrated that cyclodextrin derivatives can be fixed permanently onto polymer surfaces by functional groups using conventional technologies of textile processing. As a result of the modification process some properties of the fibres are directly influenced. But also special effects may be obtained by complexing specific chemical substances, because the fixed cyclodextrin cavities do not loose their complexing power. Conceivable fields of application are medical or technical textiles and textiles for clothing.

1. INTRODUCTION

As a last step in textile processing a finish is done to get materials of specific quality [1]. A new concept for the modification of synthetic and natural fibres is based on the permanent fixation of supramolecular components, e.g. cyclodextrins, on the surfaces by functional groups using common technologies of textile processing [2,3]. The properties of the polymers may be directly influenced by the modification process. But also the fibres achieve new and particular properties by means of the inclusion of non-polar organic molecules into the fixed cyclodextrin cavities. Such effects are not obtainable by conventional finishing methods.

In the following conditions for the application of cyclodextrins and methods for the detection of the ligands on fibre materials will be discussed. Some examples for the textile properties attainable will be demonstrated.

2. MATERIALS AND METHODS

2.1. Materials

The cyclodextrin (CD) derivatives used are development products of *Wacker-Chemie GmbH* (abbreviations and average substitution degrees in brackets): monochlorotriazinyl- β -CD (MCT- β -CD, 0.4), dihydroxypropyl-ethylhexylglycidyl- β -CD (DHP-EHG- β -CD, 0.65/0.34), hydroxypropyl-butylglycidyl- β -CD (HP-BG- β -CD, 0.63/0.32), hydroxypropyl-hydroxyhexyl- β -CD (HP-HH- β -CD, 0.43/0.41), hydroxypropyl-phenylglycidyl- β -CD (HP-PG- β -CD, 0.90/0.35), *o*-cresylglycidyl- β -CD (*o*-CG- β -CD, 1.5), ethylhexylglycidyl- β -CD (EHG- β -CD, 1.4), hydroxypropyltrimethylammoniumchloride- β -CD (HPTMAC- β -CD, 0.5).

Fabrics of cotton, regenerated cellulose (CV), polyethylenterephthalate (PET), polyamide-6.6 (PA-6.6) and polyacrylonitrile (PAN) are used as textile materials. All fabrics have been purified from accompanying substances.

2.2. Methods

Cotton samples are dipped into an alkaline solution (20 g/l sodium carbonate) of MCT- β -CD (20 g/l) at 25 °C and squeezed out under defined conditions. The fixation step is varied as follows: treatment with saturated steam (5 min at 100 °C), dry heat (5 min at 130 °C) or contact heat (3 min at 150 °C) or storage with exclusion of air (15 h at 25 °C or 4 h at 80 °C). Also cotton and CV fabric are printed with MCT- β -CD following a conventional reactive printing process (printing paste consisting of 40 g MCT- β -CD, 75 g urea, 20 g sodium hydrogen carbonate, 25 g alginate thickener and 840 g deionized water). The prints are dried (2 min at 100 °C) and fixed with saturated steam (8 min at 100 °C). All treated cellulose samples are rinsed with hot and cold deionized water.

Nonionic CD derivatives are applied to synthetic materials according to conventional exhaust dyeing methods for disperse dyes. The starting concentration is $5 \cdot 10^{-5}$ mol CD/g material and the liquor ratio is 1:50. The system is heated up with a constant rate (2 °C/min) to 130 °C (PET) or 100 °C (PA-6.6 and PAN). The total time of the treatment is 100 min. The cationic derivative HPTMAC- β -CD is applied to PAN fabric under the conditions of a basic dyeing process. The starting concentration is $5 \cdot 10^{-5}$ mol CD/g material and the liquor ratio is 1:50. The system is heated up with 2 °C/min to 80 °C and further with 0.7 °C to 95 °C. The total time of the treatment is 80 min. All samples are rinsed with hot and cold deionized water.

MCT- β -CD is directly detected on cellulose fibres by reflectance measurements in the UV region. PAN fabric which is treated with HPTMAC- β -CD is stained with the anionic indicator dye bromophenol blue ($1.5 \cdot 10^{-4}$ mol/l) in acidic solution (pH 3, acetic acid) at 25 °C, rinsed and investigated spectroscopically. Nonionic CDs are detected on synthetic

fibres by the interaction with the anionic fluorescence dye ANS (ammonium salt of 8-anilino-naphthalene-1-sulfonic acid). Samples are treated with aqueous solutions of ANS (10^{-4} mol/l) for 15 min at 25 °C, squeezed out under defined conditions and dried. The fluorescence intensity of the fabrics is determined with a spectrofluorometer RF-5001PC (*Shimadzu*).

The modified fabrics are characterized as follows: a) 10 μ l of water are put onto the polymer surface from a constant distance and the time for penetration is determined. b) C.I. Reactive Red 123 is applied to PET according to a normal reactive dyeing process. The fabric is dyed (starting dye concentration 50 mg/g) in presence of 50 g/l sodium sulfate at 40 °C. After 30 min 15 g/l sodium carbonate are added. The dyeing is continued for 80 min and the samples are rinsed with cold deionized water. c) The fabrics are treated with iodine vapour in a closed chamber during 2 h at 25 °C.

All absorption and reflectance measurements are done with a Cary 5E spectrophotometer (*Varian*).

3. RESULTS AND DISCUSSION

In **Table 1** feasible interactions between fibre polymers and chemicals of processing (e.g. dyes) are depicted. Considering those mechanisms CD derivatives have to meet some structural requirements for a successful fixation on polymer surfaces by conventional methods of dyeing. In the following several examples are discussed in detail.

TABLE 1. Interactions between fibre polymers and chemicals of processing (+ feasible interactions, - unfeasible or weak interactions; PES = polyester)

Fixation mode	Fibre material				
	cellulose	wool	PA	PES	PAN
ionic interactions	-	+	+	-	+
covalent bonds	+	+	+	-	-
van der Waals interactions	-	-	+	+	+

Cellulosic materials are treated with MCT- β -CD according to conventional reactive dyeing processes. The reaction mechanism is a nucleophilic substitution of the chlorine atoms at the CD triazine rings giving covalent bonds with cellulose. The successful application is proved by UV spectroscopic measurements. MCT- β -CD shows a strong absorption band between 220 and 260 nm. The fixation yield of the ligand depends on the fixation conditions. Best results are obtained by treating the impregnated fabrics at temperatures between 120 and 150 °C. High humidity should be avoided because of the competing hydrolysis of the reactive sites. Another possibility is to apply MCT- β -CD at

cellulose surfaces by means of common reactive printing systems. The ligand cannot be removed from the fibres even by numerous washing processes.

Hydrophobic polymers (PET, PA-6.6, PAN) are impregnated with nonionic CD derivatives which contain substituents of partly hydrophobic character using conventional methods of disperse dyeing. The permanent fixation of the ligands is based on diffusion of ring substituents into the fibres forming hydrophobic interactions. The ligands are detected on the fibres by means of interactions with the anionic fluorescence dye ANS. Dye fluorescence depends on the surroundings and is increased by inclusion into the hydrophobic CD cavities. Concerning PET fabric best results are obtained by treatment with DHP-EHG- β -CD or HP-HH- β -CD according to a common exhaust dyeing process at 130 °C. The fixation yields on PAN and PA-6.6 fabrics are less compared to PET, but normally this is the same with disperse dyes. Another possibility is the reaction of such fibres which contain ionic end-groups with counter-ionic CDs corresponding to basic or acid dyeing processes. As an example the successful fixation of HPTMAC- β -CD on PAN is proved by the interaction of the ligand with the anionic indicator dye bromophenol blue.

Some properties of the polymers may be directly influenced by the CD modification process, e.g. hydrophily, physiological and electrostatic behaviour, reactivity and complexing power. In **Figure 1** the wettability of PET fabric which has been treated with different nonionic CD derivatives is demonstrated. The hydrophily of the material is influenced significantly by kind and number of the substituents combined with the applied CD rings. The penetration time of a drop of water into the fabric is decreased drastically after impregnation with water soluble or emulsifiable CDs compared to the untreated material. On the other hand the interaction with hydrophobic derivatives like EHG- β -CD increases the hydrophoby of the polymer.

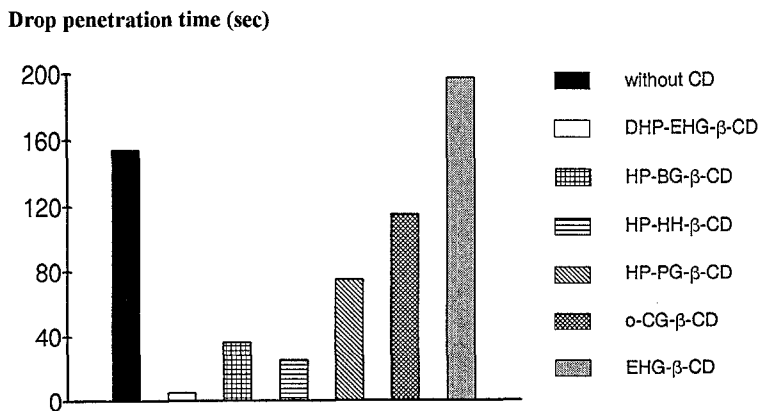


Fig. 1 Wettability of PET fabric

The application of CD derivatives causes a change of reactivity of the polymer surfaces. As an example this is demonstrated with reactive dyeings on PET fabric. **Figure 2** presents the absorption spectra of untreated and modified PET samples dyed with C.I. Reactive Red 123 according to a common reactive dyeing process. The untreated material is only slightly stained by the dye, but the dyeability of the modified fibres is significantly enhanced. This is caused by the increased number of reactive hydroxyl groups at the surface. The lower dyeability of PET treated with EHG- β -CD compared to PET impregnated with o-CG- β -CD is attributed to the less efficient wettability of the fibres (see **Figure 1**).

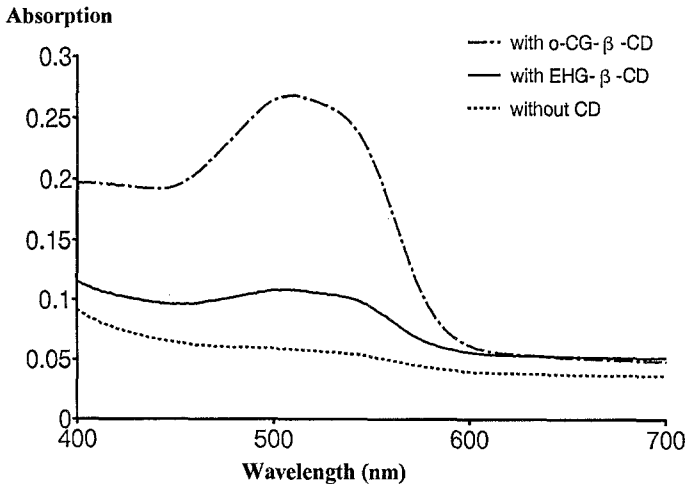


Fig. 2 Absorption spectra of PET fabric dyed with C.I. Reactive Red 123

To demonstrate the complexing power of the fixed CD cavities iodine vapour is used as a model system for building up inclusion complexes. The brown iodine colour is directly detected on the fabrics by spectroscopic measurements. It is observed that the samples which are treated with CDs absorb a higher amount of iodine compared to the untreated material. Also the host molecules are more slowly released from the modified fibres. So by the fixation at polymer surfaces the CD cavities do not loose their capability to complex non-polar organic molecules.

4. CONCLUSION

CD derivatives can be fixed permanently onto polymer surfaces by functional groups using simple methods of textile processing. As a result of the modification process some properties of the fibre materials are influenced. The fixed cavities do not loose their complexing power so that special effects may be obtained by forming inclusion complexes with specific chemical substances. On the other hand components of sweat or dirt can be disguised during the use of the treated fabrics. The fields of application for the new functional textiles are manifold, but the main purpose is to stabilize sensitive

substances or to control the release and increase the biological availability of active agents (e.g. on medical textiles) by complex formation with fixed CDs (see **Table 2**).

TABLE 2 Some possible fields of application for CD modified textile materials

Complexed substance	Field of application		
	clothing	medical textiles	technical textiles
fungicide, bactericide		x	x
perfume	x		
pharmaceutical active agent		x	
UV absorbent	x		x
insect repellent agent	x		

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