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Functional substrates for the gradual release of agents

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ABSTRACT

This work describes the functionalization of a natural and a man-made textile substrate, namely cotton and polyamide 6.6, with inclusion agents, β-cyclodextrins (β-CDs) that are able to release gradually to the user active ingredients. In this study we used aescin (*aesculus hippocastanum* extract), which is a natural agent with benefits for the treatment of varicose veins.

^{1}H NMR and UV–vis data supported the role of β-CDs as an aescin complexing agent, and the covalent nature of the linkage between β-cyclodextrins and the textile substrates, which showed a wash fastness to more than 45 washing cycles.

1. Introduction

$^{-1}$Cyclodextrins (CDs) belong to the family of cyclic oligosaccharides, resulting from the linkage of several glucose units and have the shape of truncated cones [1]. Its most interesting property is the ability to include within its hydrophobic cavity different molecules (vitamins, colorants, flavorings, essential oils, among other compounds) [2].

Among the various natural CDs (α-, β-, γ-, corresponding, respectively, to the union of 6, 7, 8 glucose molecules), the β-CDs expresses the relatively unusual characteristic of exchanging water with the environment in a quick and very effective way, which allows to form stable inclusion complexes with a wide variety of molecules [3]. Hydrogen bonds, van der Waals interactions or hydrophobic interactions have been proposed as the interaction forces between the CDs and the encapsulated molecules [4].

One requirement for a favorable complexation is the size of the molecule to be encapsulated, which must be compatible with the size of the β-CDs cavity. Another requirement is the polarity of the encapsulated molecule that must be hydrophobic, or contain hydrophobic parts. The competition with others compounds in the environment can also influence the complexation process. These limitations reduce the number of active principles, fragrances and other molecules that can be used for the complexation with CDs. Additionally, the different types of CDs show different capacities to form inclusion complexes due to stereochemistry limitations [5].

As we can see in Table 1, the cavity diameter increases considerably from α- to γ-CDs, as does the solubility in water at 25 °C. This increment in solubility can be one factor of decision when we need to choose between the different types of cyclodextrins, for instance to increase the cellular permeability of different active principles.

The process of complexation is showed schematically in Fig. 1. In general terms, the CDs are called the Host compounds and the molecule that will be included in the CDs is called the Guest. These types of interactions are designated as Host–Guest interactions.

Among all the CDs the aspect that makes the β-CDs so attractive is the fact that they are one of the few complexing agents with unlimited availability and low cost, being usually produced by enzymatic hydrolysis of starch. On the other hand, they have no toxicity and are biologically degradable, glucose being the main degradation product [5].

Due to the large availability and non-toxicity, in the last decade, several advances were observed in the development of encapsulated substances in CDs, and specifically in the textile area, most of the performed studies concern the encapsulation and release of aromas [6]. CDs were also reported as forming complexes with detergent molecules [6]. Thus, they can be considered as a new class of auxiliary substances for the textile industry, with associated advantages, including greater efficiency of the detergents and a reduction in the water used for washings. CDs can be used in washing processes for the removal of active agents retained on the fiber surface and can also form complexes in aqueous solution with the dyes used in dyeing processes, removing the fiber unfixed dyes in the subsequent washing step [7]. Other examples include the application of CDs for the removal of sweat [3,6].

One of the most important requirements for textiles is the washing fastness property. To ensure a high wash fastness, there must be a covalent linkage between finishing products (inclusion agents,

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Table 1
Principal properties of the different cyclodextrins types (adapted from [1]).

Type of Cyclodextrin	Number of glucose units (angstrom)	Cavity diameter (angstrom)	Cavity depth (angstrom)	Solubility in water at 25 °C (%)	Molecular weight (Daltons)
Alpha cyclodextrin	6	4.5	7–8	14.5	973
Beta cyclodextrin	7	7.0	7–8	18.5	1135
Gamma cyclodextrin	8	8.5	7–8	23.2	1297

β-CDs) and textile substrates (polyamide and cotton/polyamide 6.6). Several methods have been reported for the grafting between CDs and the formation of CDs polymers.

The crosslinking reaction between CDs is well documented, but the information is very scarce with respect to the covalent binding between β-CD and textile substrate surfaces. Epichlorohydrin is largely used for covalent bounding between epichlorohydrin epoxy groups and CDs hydroxyl groups.

Polyamide 6.6 fibers have a low reactivity with the most commonly used finishing agents, justifying the need for their functionalization. Several studies have shown that a pre-hydrolysis in acidic conditions can promote a partial hydrolysis of the fiber surface, generating reactive amine and hydroxyl groups, available for the coupling reaction with β-CDs [8] (Fig. 2).

In the cotton substrates there is no need to perform a pre-treatment step due to the presence of hydroxyl groups at the substrate surface.

This study describes the use of β-CDs covalently attached to textile substrates that are able to release gradually a natural ingredient, *aescin*. The desired amount of cyclodextrins on textile substrates was determined having as basis the recommended daily amount of *aescin* to achieve the reduction of inflammation of varicose veins. Several characterization tests were performed to confirm the covalent attachment of β-CDs and the capacity to encapsulate the natural active agent.

2. Material and methods

2.1. Materials and chemicals

The β-CDs used in this study were supplied by Roquette (Kleptose®) and Epichlorohydrin was supplied by Fluka. α-Bromoacrylamide (Lanasol Red) was supplied by Sigma Aldrich. All other chemicals used were of analytical grade. Polyamide 6.6 (85% polyamide 6.6 and 15% elasthane) and cotton substrates (72% cotton, 24% polyamide 6.6 and 4% elasthane) were provided by a Portuguese textile manufacturer.

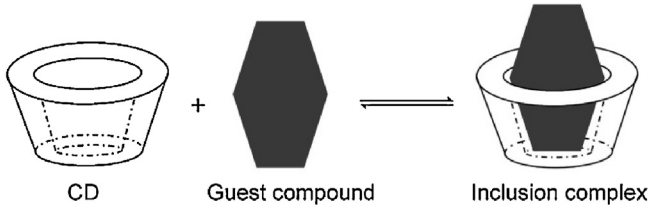

Fig. 1. Schematic representation of inclusion complex formation, adapted from [2].

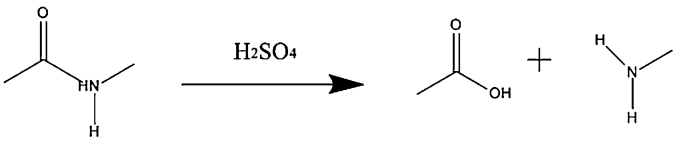

Fig. 2. General form of polyamide 6.6 degradation in the presence of strong acids.

2.2. Textile substrates functionalization

Polyamide 6.6 substrates were treated with 1 M sulphuric acid for 15 min, at 30 °C. After this activation procedure, the substrate was removed and washed with running water. The CDs were dissolved in 30% NaOH. After dissolving the CDs, a 1.60 M epichlorohydrin solution was added together with the substrates—polyamide 6.6 and cotton, using a bath ratio of 1:20 (kg/L). The substrates were kept in the reaction medium for 20 min at 40 °C and 100 rpm of stirring. After this period of time, the textile substrates were removed and washed with 2 g/L of standard detergent (phosphate-free type B) at 40 °C for 1 h and left to air dry.

2.3. Washing fastness evaluation

Washing fastness was determined, according to an adaptation of ISO 6330:2000. Several washing cycles were carried out on a Mathis Labomat BFA (Werner Mathis AG) equipment, using 4 g/L of a standard detergent (phosphate-free type B, without optical brightener), a bath ratio of 1:20 and 20 rpm of stirring, with the addition of one metallic sphere per 100 mL of bath to simulate the mechanical abrasion. Washing cycles were performed at 40 °C for 30 min (thermal gradient of 3.5 °C/min). The functionalized and washed substrates were then tested to quantify the amount of β-CDs covalently attached to the textile substrates (see Section 2.5).

2.4. Quantification of the amount of primary amine groups formed during the hydrolysis step

The amount of primary amine groups formed during the hydrolysis step was determined using Lanasol Red, a reactive dye. About 0.2 g of polyamide 6.6 were immersed in 5 mL of Lanasol Red solution and 2.6 mL of 3.4 M NaCl solution were added. Samples were then left in a thermostatic bath at 40 °C for 30 min with 130 rpm of stirring. After that time, the samples were washed with standard detergent and distilled water for 30 min at room temperature, until no more dye was released into the washing bath.

2.5. Quantification of cyclodextrins attached to the textile substrates

The amount of cross-linked CDs was quantified using an internal method, based on the complexation with phenolphthalein. A calibration curve was drawn for each textile substrate. Afterwards, both treated and untreated samples of a given weight were placed in a carbonate buffered solution with a known amount of phenolphthalein. The decrease in color intensity of the indicator solution correlates with the amount of cross-linked CDs. Absorbance was measured at the maximum absorption wavelength of phenolphthalein (550 nm) using an UV-3000 reflectance spectrophotometer (Shimadzu).