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1 Biofunctional Wool using β -Cyclodextrins as vehiculizer of Citronella Oil

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3 Fabricio Maestá Bezerra^a, Óscar García Carmona^b, Carlos García Carmona^b,
4 André Mathias Souza Plath^c, Manuel Lis^b.

5 a Department of Textile Engineering, Federal University of Technology—UTFPR-AP
6 (corresponding author: fabriciom@utfpr.edu.br)

7
8 b INTEXTER-UPC, C/Colom, 15, 08222 Terrassa, Barcelona (oscargarciacarmona@gmail.com;
9 carlos.garcia.carmona@gmail.com; manuel-jose.lis@upc.edu

10
11 c Federal University of Technology—UTFPR-LD (andre.plath@ao.com)
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13 Abstract

14 The use of biopolymers such as cyclodextrin in textiles for the development of
15 biofunctional fabrics is an alternative for the development of eco-friendly
16 textiles. Cyclodextrins can create covalent interactions with the chemical groups
17 available in wool, allowing the sorption of active molecules that will be released,
18 such as the citronella oil. Therefore, this work investigates the formation of
19 cyclodextrin complex oil applied in wool and its release mechanism. The
20 complexes obtained and the grafted fabric were characterized by TGA, DLS,
21 FTIR-ATR and SEM. The release of citronella oil was also analyzed and
22 mathematical adjustments were performed using the equation of Korsmeyer-
23 Peppas to verify the release mechanism. The results have indicated the
24 formation of the complex and its fixation by covalent bonding, according to the
25 FTIR-ATR specter and the SEM, and these have shown an anomalous release
26 profile. For this reason, the application of the complexes in wool fabrics has
27 shown to be an option in the production of eco-friendly biofunctional materials
28 for controlled release, allowing the oil properties to be used in textile matrices.

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30 **Keywords:** Biofunctional textile; cyclodextrin; citronella oil; drug delivery.
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1 **1. Introduction**

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The application of biopolymers in textiles has attracted industrial and scientific interest due to the possibility of production of synthetic products [1].

One of the most promising biopolymers is cyclodextrin (CD). According to Matioli et al. [2], cyclodextrins are produced from the starch by the cyclizing reaction of linear chains of glucopyranosides, using the enzyme cyclodextrin-glucanotransferase (CGTase).

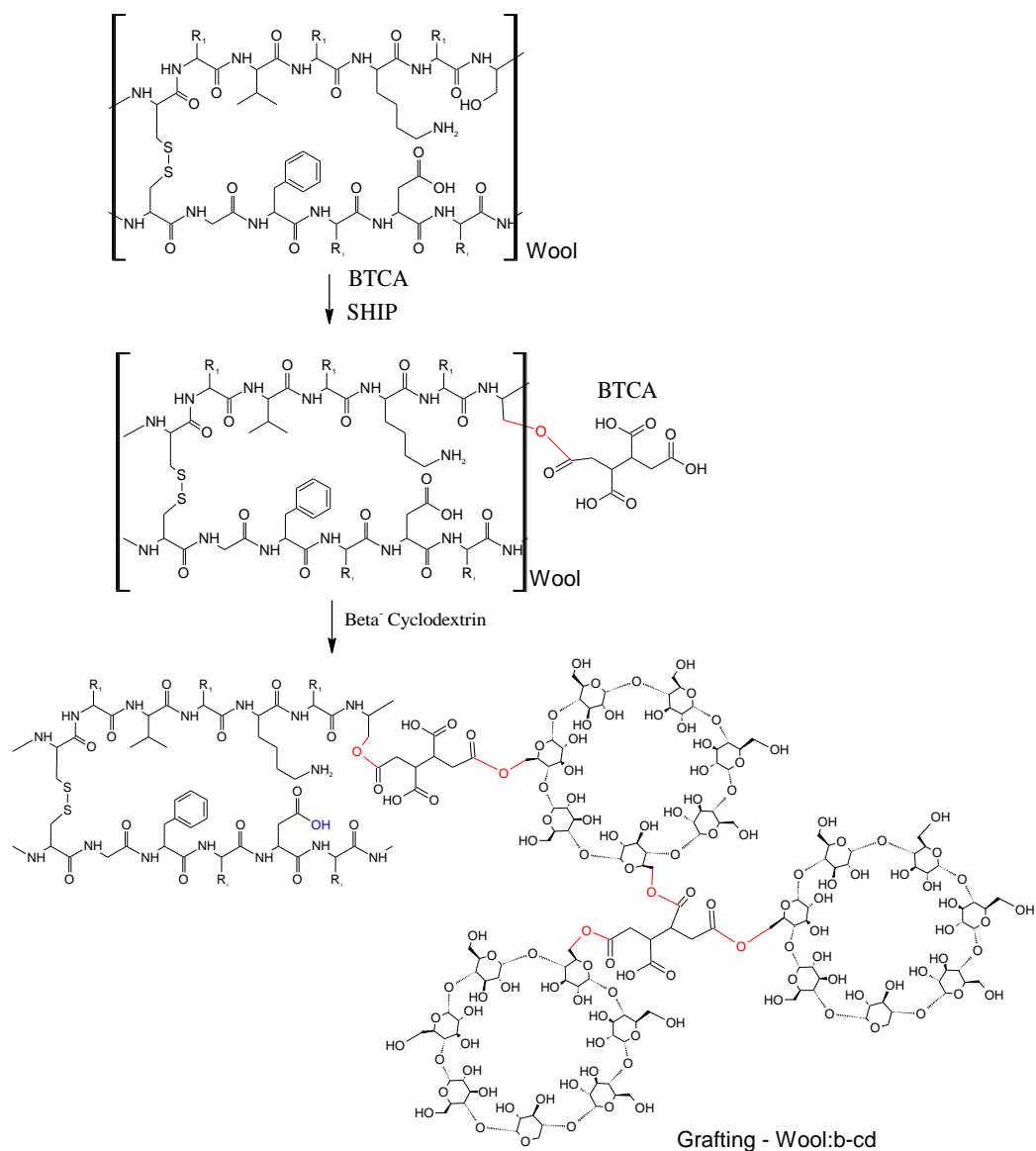
In the field of textile finishing, CDs can be applied into the surface of the textile substrate, allowing its properties to become intrinsic to the fiber. Their use fosters immediate opportunities for the development of products that are less harmful to the environment, besides having a great potential in many applications [3], being able to absorb unpleasant odors, release essential oils, vitamins, caffeine, menthol, and biocides [4-6]. CDs can form inclusion complexes with bioactive molecules, protecting them against oxidation, enhancing the chemical stability and reducing or eliminating eventual losses by evaporation [7,8].

Regarding the interactions between cyclodextrins and the textile fibers, we can cite two distinct interactions: (i) physical bonding and (ii) covalent bonding. The second type of interaction shows better durability [9]. Many textile fibers were already used as a support for cyclodextrin, such as cotton [6,10], polyester [11,12] and wool [13,14]. One of the most popular fibers, which is nowadays employed in textile products of high quality, is wool [15], a protein fiber consisting mainly of keratin [16]. Due to the protein structure, wool has many different chemical groups, such as OH, NH₂, COOH, etc. This diversity

1 allows the interaction with a diverse range of biopolymers, satisfying the
2 concern of the textile industry in raising the number of eco-friendly finishing [17].

3 The presence of hydroxyl groups in the wool fiber allows the
4 esterification reaction between the carboxyl group of the crosslinking agent
5 and the hydroxyl groups of the fiber and of the cyclodextrin. Fig. 1 represents
6 the mechanism of fixation of β -cyclodextrin (β -CD) in the wool fiber via
7 esterification [18]. The β -CD is the most widely used cyclodextrin in
8 complexation with several classes of compounds, and this is due to the
9 diameter of the cavity of this β -CD, which allows a stable inclusion with a large
10 part of the bioactive molecules.

11 Haji et al. [13] highlight that this process is possible using the reactive
12 derivative of cyclodextrins or reticulation agents, of which we can emphasize
13 the compounds dimethylol urea and polycarboxylic acids such as acid 1,2,3,4-
14 butane-tetracarboxylic (BTCA) and citric acid (CA).



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2

3 **Fig. 1.** Grafting β -CD into hydroxyl groups of wool via 1,2,3,4-butane
4 tetracarboxylic acid (BTCA) as crosslinking agent and sodium hypophosphite
5 (SHIP) as catalyst

6

7 With the fixation of cyclodextrin on the surface of the textile product,
8 grafting, the textile substrate starts to present sorption capacity and capacity for
9 the liberation of active molecules [13] such as drugs [19,20], fragrances [4,7]
10 and flavoring agents [21,22]. Peila et al. [23] point out that there is a need for
11 encapsulation of the active principle to increase the period of action, allowing a
12 more durable protection effect.

1 With the capacity to host the molecules through the applied biopolymer,
2 the textile article might become a biofunctional fabric employed in the fight
3 against vectors, depending on the encapsulated molecule. The most commonly
4 employed agent for articles with repellent properties is DEET (M-Diethyl-3-
5 methybenzamide); however, some studies point out that the employment of
6 DEET may present human toxicity with lesions that vary from mild to severe
7 [24].

8 For this reason, it is necessary to utilize products both efficient and
9 harmless to human health. Considering this, the use of bioactive compounds
10 such as essential oil of citronella (OC) has shown to be interesting due to its
11 antioxidant, antifungal, antibacterial and insect repellent properties that are
12 attributed to the molecules of geraniol and citronellal [25]. Solomon and
13 collaborators [26] point out that the use of essential oils as repellents has little
14 or no harmful effects. The author further explains that the microencapsulation of
15 citronella oils has, as its main advantage, the reduction of the oil volatility in
16 comparison with topical preparations, constantly supplying the oil to the skin.

17 In this context, the fixation of β -CD in textile articles was extensively
18 studied [6, 10-13,27,28] using the widest range of host molecules. However,
19 few studies were performed to investigate the release mechanisms of the active
20 principle encapsulated in a textile matrix. For this reason, this work has as
21 objective to present the controlled liberation kinetics of the essential oil of
22 citronella complexed by β -CD, bonded to wool fibers.

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2. Methodology

2.1. Materials

For the preparation of the complexes, β -cyclodextrin was utilized as biopolymer (Sigma Chemical, Germany) and essential oil of citronella (WNTf, Brazil) as bioactive host molecule. The complexes were applied into standard fabric 100% wool (100% WO) (Style 537, 3.68 oz/yd², ISO 105-F01) via esterification, using as reactants butane 1,2,3,4 tetracarboxylic acid (BTCA) (Sigma Chemical, Germany) and sodium hypophosphite (SHPI) (Synth, Brazil).

2.2. Methods

2.2.1. Preparation of the Complex

The methodology employed to prepare the complexes of β -cyclodextrin and citronella essential oil was adapted [8,22,29,30].

A solution was prepared with 50 mL of ethanol and water (volumetric ratio, v:v, equal to 1:3) and 3 g of β -CD. The product was emulsified using Ultraturrax (T-25) under stirring at 18,000 rpm during 5 minutes and at 60 °C, in accordance with the methodologies proposed by Wang and Cheng [8] and Oliveira et al. [30].

After this step, citronella oil was added with a rate of 9 mLh⁻¹, for a period of 20 minutes, maintaining a volumetric per mass ratio (v:m) equal to 1:1 of oil and β -CD, as shown by the work of Partanen et al. [22]. The temperature was kept at 40 °C, under stirring at 10,000 RPM for 2 hours as the methodology

1 adopted by Medronho et al. [29]. As a product, the complexes were obtained in
2 solution.

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4 *2.2.2. Thermogravimetric Analysis (TGA)*

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6 The analysis of the thermal stability of the complexes was performed
7 using the thermogravimetric equipment TGA.SDTA851 – Mettler Toledo and the
8 Software STARe (Version SW 9.01). The thermal behavior of the following
9 products was verified: citronella essential oil, β -CD and complexes (CD:
10 citronella). The method employed used a heating rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$, and a
11 temperature range from $30\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ in an atmosphere of nitrogen.

12

13 *2.2.3. Diameter Estimation using Dynamic Light Scattering (DLS)*

14

15 The Dynamic Light Scattering method was applied to determine the size
16 of the complexes using the equipment Nanoplus (EDS) and the software
17 Nanoplus Common. It were performed 70 accumulations for each sample. The
18 experiments were executed at a single angle of 90° , static measurement.

19

20 *2.2.4. β -CD grafting on wool*

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22 The application of the complexes on the surface of the fabric was
23 executed using the pad-dry technique with a *foulard*, as presented by Dehabadi
24 et al. [31]. The process was followed by drying at room temperature [32]. The
25 wool fabric (15x5 cm) was impregnated for 1 minute in 100 mL of water solution
26 containing 60 gL^{-1} of complexes, 6 gL^{-1} of butane 1,2,3,4 tetracarboxylic acid
27 (BTCA) and 6 gL^{-1} of sodium hypophosphite, at a temperature of $25\text{ }^{\circ}\text{C}$ and pH

1 6. After this, the samples went through a *foulard*. The working pressure used
2 was 2 bar to obtain a pick-up of 120%. Finally, the drying and curing were
3 carried out at a temperature of 170 °C for 3 minutes.

4 The yield of the application of the β -CD was calculated using the mass
5 gain of the wool fabric after the polymerization. This result was called grafting
6 percentage yield (G%), according to the Equation (1) [13]:

$$G(\%) = \frac{M_2 - M_1}{M_1} \times 100 \quad (1)$$

7 Where M_1 and M_2 are the masses before and after the grafting,
8 respectively.

9

10 2.2.5. *Finishing evaluation*

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12 The application of the complexes was also evaluated using Scanning
13 Electron Microscopy (SEM, JEOL-JSM 5610), Fourier Transform Infrared
14 Spectroscopy (FTIR) and Attenuated Total Reflection (ATR), Frontier – Perkin
15 Elmer, with a resolution of 1 cm^{-1} and 64 accumulations, with a range in the
16 infrared spectrum between 650 and 4,000 cm^{-1} . Both techniques (SEM and
17 FTIR-ATR) were carried out on the wool fabrics with and without the finishing.

18 The wash durability of the functionalized wool was verified by SEM after
19 subsequent wash cycles-up to 2 cycles (5 washes each cycle). Washing was
20 carried out in accordance with the AATCC Test method 61-2007-2A.

21

22 2.2.6. *Cytotoxicity assay*

23 The cytotoxicity of the fabrics treated with the complexes was evaluated
24 by Trypan Blue in fibroblast. This test evaluates the damage to the cell
25 membrane. The fibroblast cell suspension at the concentration of 1.5×10^5 cells

1 /mL was distributed on 24 wells plates, 500 µl/well, cultured medium containing
2 10% FBS and antibiotics.. The cell were incuated for 24 h at 37°C and 5% CO₂.
3 After the incubation period, a 100 µL aliquot of the cell suspension was
4 withdrawn and diluted in trypan blue (0.4%, Sigma®). The color intensity was
5 measured at optical microscope. The experiments were performed intriplicates.
6 The percentage cell viability was then calculated as follows, Equation (2):

$$\text{Cell viability (\%)} = \left(\frac{\text{viable cells}}{\text{total cells}} \right) \times 100 \quad (2)$$

7 *2.2.7. Quantification and mathematical adjustment of the controlled release of*
8 *citronella oil*

9
10 The liberation profiles of the complexes supported by wool were
11 determined using a technique presented in a previous work [33]. The wool
12 fabric, before the application of the treatment, was taken to a temperature
13 controlled bath at 37 °C ± 0.5 °C, under stirring on a shaker WNB14 Memmert.
14 Aliquots of 2 mL were drawn at predetermined times and filtered (1.5 µm). The
15 absorbance was determined using UV spectroscopy UV-240LPC – Shimadzu,
16 333 nm (OC). The obtained data were adjusted using the equations proposed
17 by Higuchi [34] and Korsmeyer-Peppas [35].

18

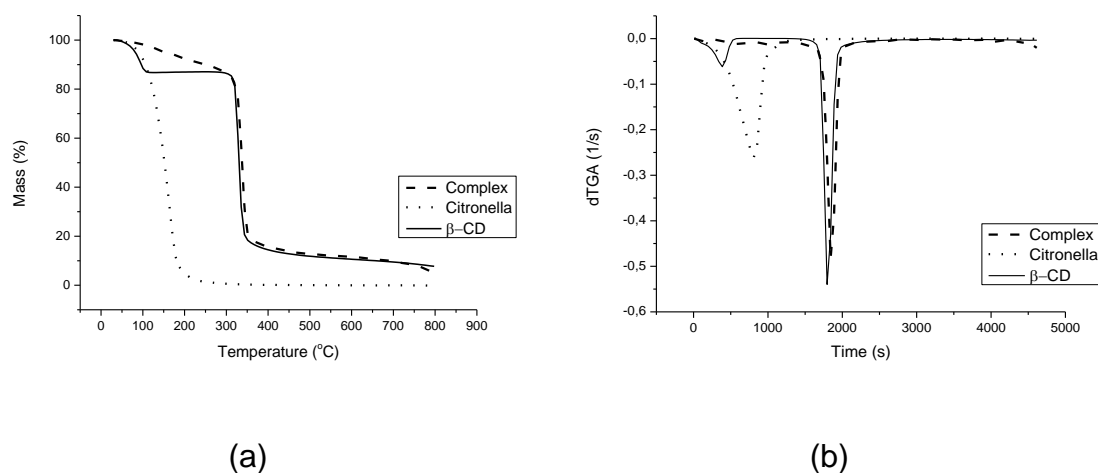
19 **3. Results and discussion**

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21 *3.1. Thermal Analysis*

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23 Fig. 2 shows the thermogravimetric curve (TG) and the first derivative of
24 this curve (DTG) of pure compounds (OC and β-CD), as well as of the complex
25 formed by them.



1 **Fig. 2.** Thermogravimetric curves (a) TG for Citronella, β -cyclodextrin and
 2 complex (b) DTG for citronella, β -CD, and complex.

3

4 Table 1 points out the main stages of mass loss with the residual
 5 percentage for each compound.

6

7 **Table 1** – Thermogravimetric data for the samples of citronella, β -CD, and the
 8 complex.

		CITRONELLA	β -CD	COMPLEX
Stage 1	ΔT_{dec}	30 – 192.5 °C	31.57 – 89.63 °C	61.3 – 108.3 °C
	T_{max}	134.48 °C	63.07 °C	100.5 °C
	$\%_{pm}$	97.8 %	13.2 %	2.13 %
Stage 2	ΔT_{dec}	-	260.57 – 340.10 °C	258.78 – 354.97 °C
	T_{max}	-	300.23 °C	308.56 °C
	$\%_{pm}$	-	71.6 %	68.8 %
Residual		0%	7.7 %	4.7 %

9 ΔT_{dec} Decomposition temperature variation

10 T_{max} Maximum Temperature

11 $\%_{pm}$ Mass Loss Percentage

12

13 As it is observed in the thermogram profiles in Fig. 2, the essential oil of
 14 citronella is decomposed at approximately 200 °C [33,36], presenting a single
 15 thermal event of decomposition and without residual percentage. However, with
 16 regard to β -CD, two distinct regions of mass loss were observed. The first one

1 extends up to 89.63 °C, corresponding to the dehydration of water molecules
2 bonded to cyclodextrin, indicating that the moisture percentage of β -CD is equal
3 to 13.2% (mass per mass ratio, m:m). This percentage of water is commonly
4 found in works that use cyclodextrin as complexing agent [37,38].

5 The second region of mass loss, stage 2, for the β -CD is a direct result
6 of the decomposition of the structure (Table 1), which shows its beginning at
7 260.57 °C and is completed at 340.10 °C. Subsequent to the decomposition
8 event, it is initiated an elementary carbon formation, carbonization [39-41].

9 Regarding the formed complex, it is noted the distinct behavior in the
10 thermogravimetric curves, Fig. 2 (a) and (b). The complex presents higher
11 thermal stability and lower presence of water, shifting from 13.2% of the pure
12 cyclodextrin mass loss to 2.13% in the complex. This fact has happened due to
13 the encapsulation of citronella, which came to occupy the place previously
14 taken by the molecules of water, as described by Venturini et al. [42]. With the
15 increase in temperature, the oil is released with the decomposition of the
16 biopolymer that protects it.

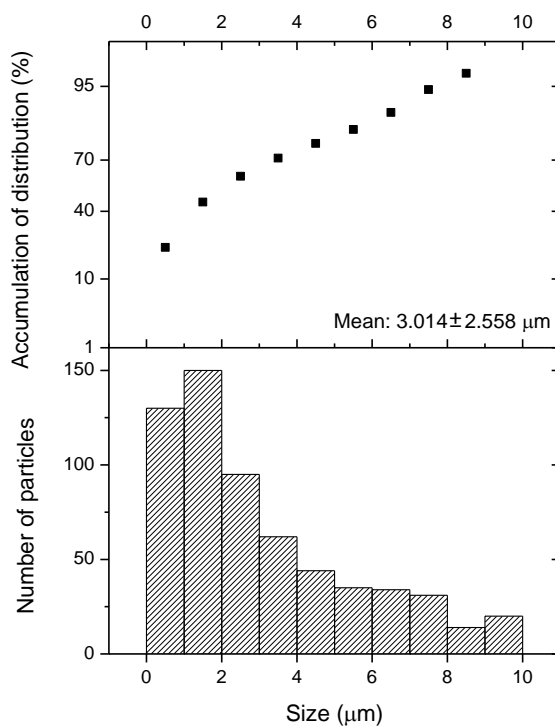
17 On the other hand, the thermal stability of the oil was improved. The
18 volatilization in regular conditions increased from 192.5 °C to approx. 340 °C
19 (Table 1). This change has also been verified by Özdemir and Gökmen [43].
20 The authors used β -CD to complex vanilla, and observed a displacement from
21 83 °C to 130 °C. From the evidence, it is possible to affirm that the β -CD could
22 have formed the inclusion complex with the OC.

23

24 *3.2. Size Distribution for the Complex*

25

1 The complexes formed were evaluated using DLS to quantify the size
 2 distribution as exhibited in Fig. 3. It has been shown that the size distribution
 3 occurs in a range between 0 and 10 μm .



4
 5 **Fig. 3.** Histogram of size distribution for the sizes of the complexes of citronella
 6 essential oil and distribution build-up.

7
 8 The average size of the complexes was $3.014 \pm 2.558 \mu\text{m}$. 57.083% of
 9 the complexes were produced within a range between 1.5 – 4.5 μm . Özdemir
 10 and Gökmen [43] point out that the size is determined by the ratio between core
 11 material and wall material, in this case, 1:1. Complexes with this dimension can
 12 more easily coat the surface of the fiber, as it will be shown in the SEM results.

13

14 3.3. *Evaluation of the grafting in wool*

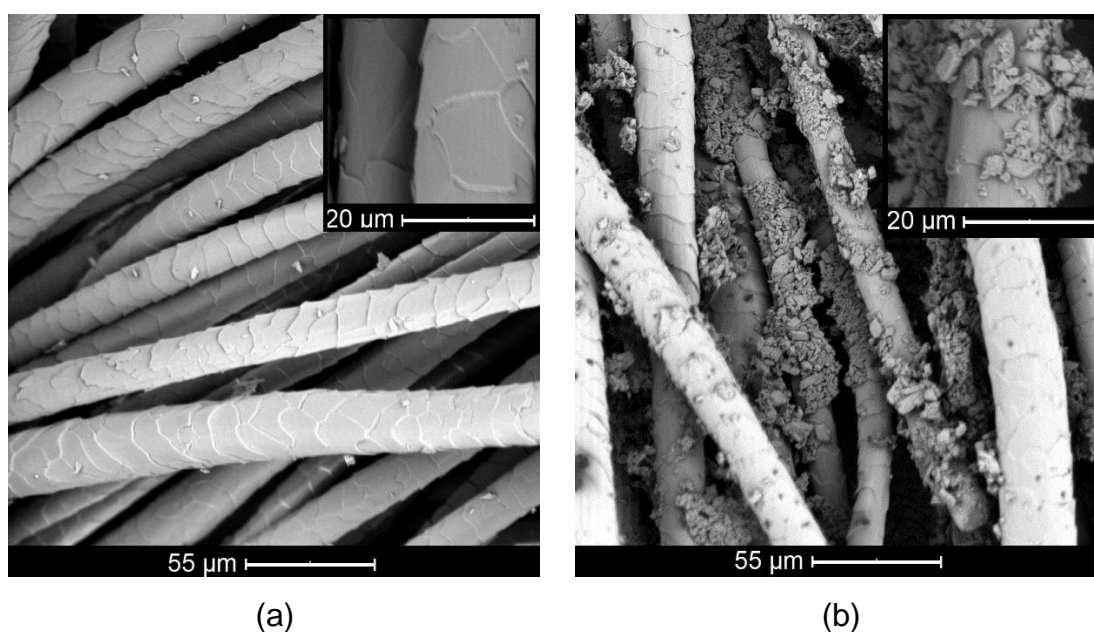
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1 Table 3 shows the percentage of grafting yield for a solution of 100 mL
 2 of water containing 60 gL⁻¹ of complexes, 6 gL⁻¹ of BTCA and 6 gL⁻¹ of SHPI.
 3 After drying and curing for 3 minutes at a temperature of 170 °C, the grafting
 4 was calculated using Equation (1).

5 **Table 3** – Determination of grafting yield, β-CD wool.

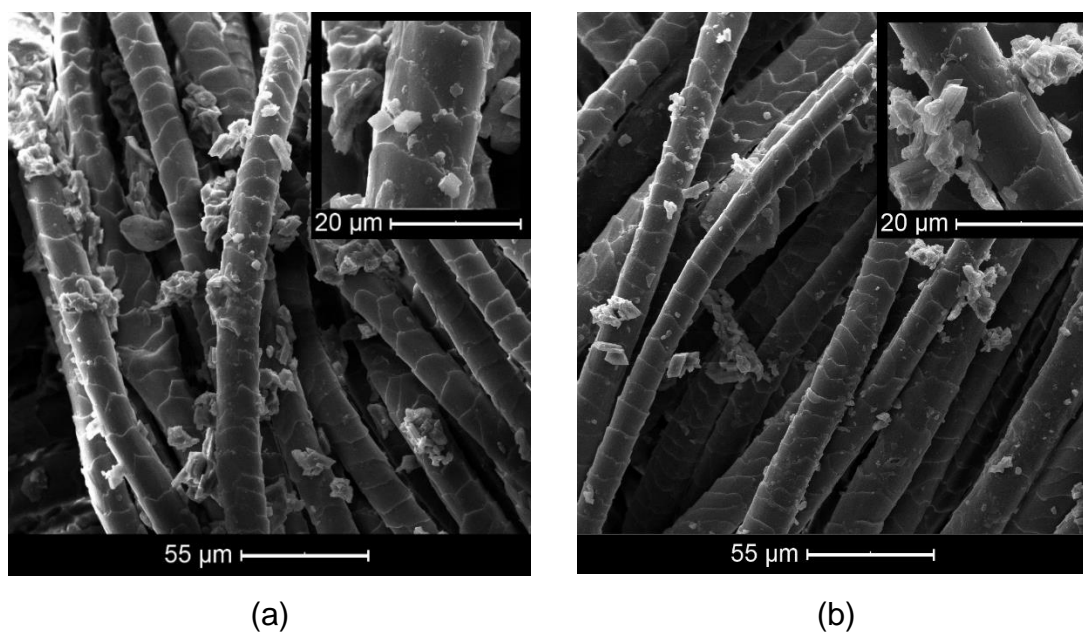
PARAMETER	WOOL
Mass (g)	0.189 ± 0.005
Dry Mass (g)	0.205 ± 0.003
%Graft yield	8.7 ± 0.091

6
 7 As shown by Shown and Murthy [28], the mass gain for the substrate is
 8 attributed to the coating of the fibers by the reaction between the biopolymer,
 9 BTCA and the wool fabric. Since the fabric has hydroxyl groups, as well as the
 10 cyclodextrin, the reaction of esterification becomes possible [13,14,18,44], as
 11 illustrated by the mechanism in Fig. 1.



12 **Fig. 4.** SEM images of the (a) untreated wool and (b) treated wool, complex (β-
 13 CD:OC) deposited on the fabric.

1
2 Fig. 4 shows the changes in the surface of the wool fiber, highlighting
3 the grafting process on the fabric. In Fig. 4 (a) it is possible to observe the wool
4 fibers without any type of treatment. The fibers in this condition have a smooth
5 structure with few structural impurities. It is noted in Fig. 4 (b) the clear coating
6 of the fiber. There is a cluster of particles, evidencing the mass increase of the
7 fabric of approx. 8%. This occurs due to the presence of β -CD on the surface of
8 the fabric; and therefore, the realization of grafting. Figure 5 shows the surface
9 of the woolen fabric after washing. It is noticed that there is a decrease in the
10 amount of complexes, however, these still cover the fiber, showing that the
11 interaction between the fiber and the complex, esterification via BTCA, has
12 been established. Khanna et al [45], shows that as the cyclodextrin is bonded to
13 wool fiber hydroxyl groups through ester linkages offering good wash
14 resistance.



15 **Fig. 5.** SEM images of the treated wool, complex (β -CD:OC) deposited on the
16 fabric, after washing (AATCC Test method 61-2007-2A): (a) 5 and (b) 10
17 washes.

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The FTIR-ATR spectrum, Fig. 6, for the wool fiber presents as main

bands: $1,079\text{ cm}^{-1}$ vibration of the functional group S=O; $1,172\text{ cm}^{-1}$ Strong C–O

stretching of primary alcohols and phenols; $1,395\text{ cm}^{-1}$ axial deformation of the

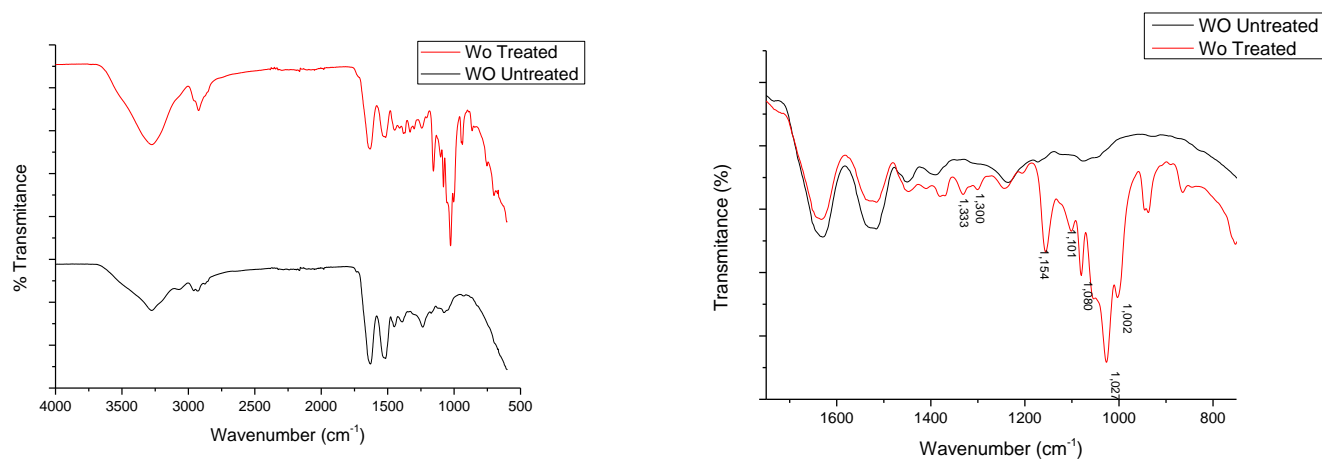
carbonyl group C=O from carboxylic acid; $1,630\text{ cm}^{-1}$ vibration of the carbonyl

functional group C=O primary amide; $3,072\text{ cm}^{-1}$ stretching, NH_2 associated

with primary aliphatic amines; $3,276\text{ cm}^{-1}$ vibration of the axial deformation of

the O–H bonding [46]. The variety of functional groups in wool comes from the

protein structure [16], allowing an interaction with many finishing products [17].



10 **Fig. 6.** Fourier Transform Infrared Spectroscopy (FTIR-ATR) for the textile

11 substrate 100% wool, treated and untreated.

12

13

New peaks are originated in the treated wool fabric in a region between

14

$700 - 950\text{ cm}^{-1}$. These peaks are attributed to the vibrations of the C–H and the

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vibrations of the C–C in the glucopyranose ring present in cyclodextrins, as

16

observed by Aguiar et al. [37] and shown in Fig. 6. This evidences the retention

17

of the complexes (β -CD: OC) above the textile substrate, as shown in Table 3.

18

Other peaks that can be noted present in Fig. 6 are in the region $1,150$

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– $1,020\text{ cm}^{-1}$ and are attributed to the stretching vibrations of C–O–C, the

1 bonding of the group's ether and hydroxyl (glycosidic bonding). The position of
 2 these bands, after the grafting in wool, can be attributed to the presence of
 3 cyclodextrin in the fiber, indicating the coating [13,14]. The appearance of a
 4 band in the region of $1,300\text{ cm}^{-1}$ is related to the ester carbonyl [47] present in
 5 the reaction between the group OH of the cyclodextrin, COOH of the BTCA and
 6 the group OH of the wool fiber.

7 **Table 4 shows the results of cell viability of untreated and treated fabrics.**

8 **Table 4 – Cytotoxicity assay**

9

	Viability (%)	Standard deviation (±)
Controle	98.296	0.788
Untreated fabric	97.886	0.824
Treated fabric	96.394	1.921

10

11 **The indicated values show that tissue with treatment has high cell**
 12 **viability, 96.394 ± 1.921 , as indicated by the authors Solomon et al [25], citronella**
 13 **and cyclodextrin pose no problem to human health when used in fabrics in**
 14 **contact with the skin.**

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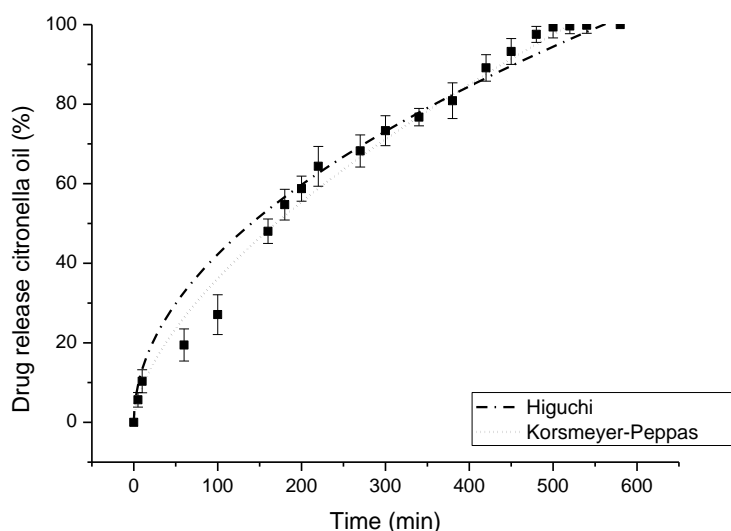
16 3.4. *Controlled Release Profile*

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18 One of the best advantages of the encapsulation of OC using β -CD is
 19 its controlled release. This property allows the enhancement of oil activity in the
 20 textile matrix, improving the efficiency of the compound.

21 Fig. 7 shows the release profile in a quantitative evaluation using UV-
 22 VIS spectrophotometer for the wool fabric coated with complexes β -CD: OC, at

1 a temperature of $37 \text{ }^\circ\text{C} \pm 0.5 \text{ }^\circ\text{C}$, under stirring. The profile shows the relation
 2 between the concentration at a given point t and the maximum concentration
 3 released ($\frac{M_t}{M_\infty}$). In this case, there is the release of the active compound followed
 4 by a plateau, indicating that the total liberation was reached [48], in the
 5 experiment, the equilibrium was reached in 600 min, as noted in Fig. 7.



6
 7 **Fig. 7.1** Profile modeling for the release of the citronella essential oil complex
 8 grafted to the wool textile substrate using the Higuchi, Korsmeier-Peppas
 9 Model.

10

11 The model proposed by Higuchi [34], Korsmeier-Peppas [35] applied to
 12 drug release can also be used to understand the controlled release of the
 13 complexes formed with cyclodextrin applied to textile matrices [49]. The
 14 mathematical equation of Higuchi that governs the system is flat (wool) and the
 15 mechanism is based on Fick's law, being possible to write it as:

$$\frac{M_t}{M_\infty} = K_H t^{1/2} \quad (3)$$

1 where $\frac{M_t}{M_\infty}$ is the ratio between the amount of release of the active principle at
2 each time point t relative and K_H is the Higuchi constant.

3 The model proposed by Korsmeyer-Peppas is generally applied to
4 analyze the discharge of polymeric dosage forms, whenever the release
5 mechanism is unknown, or when more than one mechanism is involved [35].

6 The krosmeier-Peppas equation can be written as follows:

$$\frac{M_t}{M_\infty} = K_{KP}t^n \quad (4)$$

7 Being K_{KP} the constant of the kinetic rate of Korsmeyer-Peppas that
8 incorporates the structural and geometric characteristics; n the exponent of
9 liberation, the indicator of the mechanism is related to the release geometry
10 [50]. If $n= 0.5$, the release occurs via Fickian diffusion mechanism, in the
11 diffusion process, the matter is transported to the core of the system, resulting
12 in random molecular movements that occur over short distances [51]; if $0.5 < n$
13 < 1.0 , the mechanism of diffusion is anomalous, anomalous behavior can be
14 considered as intermediate between the Fickian and non-Fickian types of
15 diffusion. According to Costa and Lobo [52], there are two important time
16 dependent processes that involve this system: the first, when occurs the
17 diffusion from the middle to the interior of the polymer, making the dry core
18 hydrated (dilation), and the second, when the external layer becomes jellified
19 and suffers erosion; and if $n = 1.0$, occurs non-Fickian diffusion, in this case, the
20 kinetics of zero order release is controlled, and the release is controlled only by
21 the phenomenon of polymer swelling (matrix relaxation or release by erosion).

22 Considering the release profile presented in Fig. 7, and the equations of
23 Higuchi (Eq. 3) and Korsmeyer-Peppas (Eq. 4), it were obtained the data
24 presented in Table 5.

1

2 **Table 5** – Modeling parameters for the controlled release of citronella oil
 3 complexed by β -CD grafted onto a wool textile matrix.

MODEL	VARIABLES	PARAMETER
Higuchi	R^2	0.9751
	K_H	0.0422 ± 0.0007
	$D_f(10^{-3})$	0.3500 ± 0.0116
Korsmeyer-Peppas	R^2	0.9877
	K_{KP}	0.0213 ± 0.0035
	n	0.6166 ± 0.0275

4 D is the coefficient of mass transport in relation to the thickness of the fabric (D/δ^2), express in
 5 s^{-1} .

6

7 Amongst the adjustments performed, the one that shows a better
 8 correlation coefficient is the one proposed by Korsmeyer-Peppas, $R^2=0.9877$
 9 and $n=0.6166 \pm 0.0275$, when compared to the Higuchi model ($R^2=0.9751$), this
 10 better fit occurs because the model assumes that the release is governed by
 11 diffusion and polymer relaxation. The exponent value n evidences that the
 12 complexed oil applied to the wool fabric presents anomalous diffusion
 13 mechanism ($0.5 < n < 1.00$) [50]. This means that the mobility of the wool chains is
 14 higher than the mobility of the oil molecules themselves. Then, the diffusion of
 15 oil molecules, governed by the concentration gradient, is being interfered by the
 16 mobility of polymer molecules.

17 Thus, there is both diffusion and relaxation of the polymer, these two
 18 steps occur simultaneously. The water molecules begin to diffuse into the wool

1 structure and, after, into cyclodextrins, they begin to interact with the hydrophilic
2 sites of the biopolymer, leading to volume expansion [53], and this reduces the
3 hydrophobic interactions of the cavity where the oil is found. Radu et al. [54], in
4 their paper on the complexation of hydrocortisone acetate applied onto cotton,
5 showed that after the swelling of the polymer, there is a decrease in the
6 hydrophobic interactions between the CD cavity and the guest molecule,
7 causing the complexed agent to be released.

8 Scacchetti et al. [49] treated cotton fabrics with complexes of β -CD and
9 thyme oil, and also obtained the anomalous release of oil ($n = 0.620 \pm 0.0220$),
10 and showed that the affinity of the exterior of the cyclodextrin (hydrophilic) with
11 water promoted the relaxation of the biopolymer chain, modifying its structure
12 and releasing the oil.

13 The controlled release following the anomalous model allows the
14 delivery of the active principle under the desired conditions, that is, it prolongs
15 the effect of the properties of the oil. The transference textile-dermis occurs
16 without the need for conscious interference of the user.

17 The liberation of active substances depends on many factors, such as
18 the diffusion of the substance through the matrix, the degradation of the
19 complexes, the morphology, concentration and distribution of the oil and, finally,
20 the hydrophilicity of the textile material [48,55,56]; therefore, the liberation
21 profile is a sum of all these effects.

22

23 **4 Conclusion**

24

25 In summary, β -cyclodextrin complexes and essential oil of citronella
26 were prepared to biofunctionalize wool fabrics. These complexes were analyzed

1 using TG and DLS. The characterizations have shown that the incorporation
2 was possible. Consequently, the complexes were applied into the fabric via a
3 reaction of esterification of the groups OH of the wool fiber, COOH of the BTCA
4 and OH of the cyclodextrin.

5 The grafting yield was obtained through the mass gain measurement
6 ($8,47 \pm 0,091$) and its effectiveness was evaluated using FTIR-ATR. The
7 technique revealed the formation of a carboxylic ester on the surface of the
8 wool fiber (bands $1300-1630\text{cm}^{-1}$). Besides, the micrographs made with SEM
9 prove the morphological modification of the wool surface, **as well as the**
10 **durability of the finish after washing.**

11 The controlled release *in vitro* allowed to evidence that the release rate
12 of citronella oil in the biofunctionalized fabric can be described using the model
13 proposed by Korsmeyer-Peppas. The diffusion in this model is anomalous,
14 meaning that the release rate depends on the molecular flow of the biopolymer
15 and the textile matrix. This fact allows the development of new finishing using
16 cyclodextrins and oils. The fabric with cyclodextrin and its surface can be used
17 as a system of adsorption and release of bioactive molecules, making possible
18 a wide range of effects such as repellency, aromatherapy, skincare, etc.

19

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