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Functionalization and characterization of cotton with phase change materials and thyme oil encapsulated in beta-cyclodextrins

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ABSTRACT

The aim of this work was to study the production of comfortable cotton plain-weave fabrics with antibacterial and antifungal characteristics through a simple finishing process, which consists in applying microcapsules of phase change materials (mPCM), monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) and thyme oil. The fabrics were characterized by Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Contact Angle and Infrared Thermography. The thyme oil release was also analyzed, as well as the antibacterial and antifungal activity. The materials treated with 20 μL/mL of thyme oil have shown anomalous oil release mechanisms, according to the Korsmeyer-Peppas model, and activity against *Staphylococcus aureus*, *Escherichia coli*, *Trichophyton rubrum*, *Pseudomonas aeruginosa* and *Candida albicans*.

Therefore, it was reached the conclusion that mPCM, conjugated with thyme oil encapsulated in MCT-β-CD, proved to be an interesting option to produce materials possessing thermoregulation properties with putative clinical relevance for the prevention of infections, particularly dermatophytosis.

1. Introduction

There is an increase in the number of studies about textiles with properties such as the ability to repel water and dirt, thermal comfort, resistance to the fire and inhibition of microorganisms, for example, looking for high quality products resulting from the combination of new materials with technologies [1,2]. Functionalization in textiles is an effective way to improve or add properties to modify their behavior. Currently, there are many studies concerning functionalized textiles, taking advantage of both the large surface area of textiles and the possibility to produce biodegradable and biocompatible structures [3–5].

The use of phase change materials (PCMs) in textiles provides a thermoregulation system, developed to regulate the variations of temperature of the human body. Hence, by ensuring to the body a comfortable temperature through the wearing of these textiles, they promote comfort to the user, especially in the unfavorable environments [6–8].

An increasingly more adopted concept for the modification of textile substrates is based on the permanent bond of compounds, such as microcapsules and cyclodextrins (CD), on the surface of the material. Among the components of the microcapsules that can be added, the highlight is for PCMs. They are characterized by having a phase change in a given temperature range, which leads to the storing or transferring of thermal energy. Due to latent heat, the microcapsules can store and release energy, which occurs without significant change in temperature allowing an insulation effect [9–11].

CD provides hosting cavities that can include a large variety of guest molecules for specific functionalities. This finishing strategy offers the textiles new properties such as antimicrobial, anti-UV, cosmetic, and others, and is particularly useful for stabilizing active agents [12,13]. They are cyclic sugars obtained through the enzymatic degradation of starch, being that α, β and γ CD with 6, 7 and 8 glucose units respectively are the most common. Nevertheless, β-CD is the widely used in textile finishing due to the more suitable cavity diameter that allows the formation of stable inclusions of complexes with a large number of compounds [14–18]. The inclusion mechanism involves the displacement of water from the hydrophobic cavity by the hydrophobic guest molecule. Host-guest complexes are energy favorable [19,20].

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Among all β-CD derivations, monochlorotriazine-beta-cyclodextrin (MCT-β-CD) is the most interesting to be utilized in cellulosic substrates due to the simple attachment process under relatively smooth conditions. Monochlorotriazinyl groups of CD react through covalent bond with nucleophilic groups, such as hydroxyl groups, of cellulose [21,22].

Superficial infections by fungi and bacteria are very common. Dermatophytic infections affect 20–25% of the world population and constitute a serious public health problem. These dermatophyte fungi metabolize the keratin present on human epidermis, hair and nails. Fungal nail infection, onychomycosis, accounts for 50% of all nail infections. *Tinea pedis,* also known as athlete's foot, is connected with highly contagious fungi. *Trichophyton rubrum* and *Trichophyton mentagrophytes* are the species more frequently involved. Yeasts, particularly *Candida albicans* and *Candida parapsilosis*, are also relevant infectious agents. Besides inflammation, the damaged tissue resulting from the infection becomes more vulnerable to bacterial infections and species such as *Staphylococcus aureus* and *Pseudomonas aeruginosa* can be involved as primary or secondary infectious agents [23,24].

Plant extracts, essential oils and their active compounds have been isolated, identified and characterized, considering the acknowledgement of the importance of plant-based materials as potentially non-toxic and non-allergenic antimicrobial materials. Several medicinal plants such as *Mentha piperita, Thymus vulgaris, Origanum compactum, Salvia officinalis, Artemisia absinthium* and *Lavandula angustifolia* have been studied [25–29]. Among these natural biocides, thyme oil (from *Thymus vulgaris* L.) has been suggested to possess high antimicrobial, phytotoxic and insecticidal properties, which can be attributed to the presence of phenolic compounds, especially thymol (5-methyl-2-(1-methylethyl)phenol) and carvacrol (2-methyl-5-(1-methylethyl)-phenol) [30–34].

Hence, the aim of our study was to prepare and characterize cotton fabrics possessing thermal comfort together with antibacterial and antifungal properties through the combination of microcapsules of PCMs, MCT-β-CD and thyme oil in a simple application process. The interest in the design and optimization of these multifunctional materials is obvious, as far as we know even to the best of our knowledge, this combination of products has never been properly analyzed in textile finishing.

2. Measurements and characterizations

The samples utilized were composed of plain-weave bleached taffeta cotton fabrics, 585 g/m^2, supplied by Textile Belém, Brazil.

In this work, the thyme oil (composed of 44.88% thymol, 20.53% *p*-cymene, 14.27% γ-terpinene, 5.98% linalool, 4.6% carvacrol and 9.74% of others components) was obtained from Soria Natural S. A. (Spain) and MCT-β-CD from Wacker

The melamine-formaldehyde (MF) microcapsules of phase change materials (mPCMs) were supplied by Micrópolis Devan (Portugal). Phenolphthalein was supplied by Panreac, Montplet & Esteban S.A., Spain.

All other reagents, such as ethanol and sodium carbonate, of analytical grade, were purchased from Sigma-Aldrich, Portugal.

2.1. Measurements

2.1.1. Functionalization of cotton with MCT-β-CD and mPCMs

MCT-β-CD were applied by conventional pad-dry-cure method. A MCT-β-CD solution (30 g/L; pH 4) was applied by impregnation in a Foulard Roaches (4 bar, 6 m/min, pick-up 90%). Samples were dried and cured in Warner Mathis AG, Stenter at 150 °C during 5 min. mPCM (300 g/L) and MCT-β-CDs (30 g/L) were applied in a single bath (pH 4) by conventional pad-dry-cure process. The samples were impregnated with solution in Foulard Roaches (4 bar, 6 m/min, pick-up 90%), dried and cured at 140 °C during 2 min. Finally, they were rinsed thoroughly using hot tap water, followed by cold tap water for 10 min and dried in air conditioning.

2.1.2. Evaluation of MCT-β-CD fixation on cotton samples

The MCT-β-CD quantification on fabrics was made indirectly, through the phenolphthalein method [18,35,36]. Succinctly, this method is based on the decrease of the absorbance of the phenolphthalein alkaline solution due to the presence of CD. Phenolphthalein can form 1:1 complexes with CD resulting in a change in color, measured with a UV-2101PC Shimadzu spectrophotometer (Kyoto, Japan).

The phenolphthalein solution was prepared by dissolving 0.1 g in ethanol (100 mL). The solution was stirred for 30 min at 30 °C. Then, a buffer solution (sodium carbonate 52.8 g/L and sodium bicarbonate 8.4 g/L; 1000 mL) was added to achieve a final concentration of $3.2e^{-5}$ M. The resulting work solution was stored and kept protected from light.

The alkaline solution of phenolphthalein (pH 10.5, 30 mL of $3.2e^{-5}$ M) was added to a flask containing a sample of MCT-β-CD-cotton fabrics (1 g). After mixing for 3 h at 25 °C, the absorbance of the solution was measured at 553 nm and the MCT-β-CD quantification was calculated according to the curve calibration previously made. Three independent measurements were made from each concentration.

2.1.3. Thyme oil application

Modified and unmodified samples with MCT-β-CD were immersed in a solution composed of ethanol/water (60:40) containing thyme oil (2%) and put under spinning during 20 min. Afterward, they were squeezed on Foulard (pick-up 90%).

The reference samples were treated with ethanol/water (60:40) solution only. After padding, the samples of fabrics were washed in tap water and dried at room temperature.

2.2. Samples characterization

2.2.1. FTIR spectroscopy

Attenuated total reflection Fourier Transform Infrared spectra (ATR-FTIR) of untreated cotton, cotton treated with MCT-β-CD loaded with thyme oil, and cotton treated with MCT-β-CD with mPCM were recorded on ATR-FTIR Avatar 360 spectrophotometer (Madison, USA). KBr windows of MCT-β-CD were made. mPCM and *Thymus vulgaris* oil were dried and analyzed using NaCl windows in the same equipment. Each spectrum was scanned 60 times with a resolution of 16 cm^{-1}.

2.2.2. DSC analysis

DSC analyses were performed with a differential scanning calorimeter Mettler Toledo DSC-822^e instrument (Giessen, Germany). Melting point and heat of fusion calibration were carried out with indium under nitrogen atmosphere (80 mL/min). A heating rate of 10 °C/min going from 25 °C to 400 °C was used to investigate the inclusion complex with MCT-β-CD.

A heating rate of 10 °C/min going from 0 °C to 50 °C was used to examine the thermoregulation effect of the fabrics containing mPCM. All the tests were performed thrice and the average values were recorded. The DSC analyses have covered random areas of each sample and an empty pan was used as the standard reference. Analyses were performed under a nitrogen purge. The weight of each sample was kept constant (5.7 ± 0.1 mg).