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A multifunctional cotton fabric using TiO_2 and PCMs: introducing thermal comfort and self-cleaning properties

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Abstract. The development of materials with multiple functionalities is a market imperative that places new challenges on textile processing. The purpose of this study was to establish the conditions to obtain a cotton material that is comfortable, with self-cleaning and antimicrobial properties. For this purpose, microcapsules of phase change materials (mPCM) and titanium dioxide nanoparticles (TiO_2 NP) were applied. The resulting fabrics were characterized with resource to infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), contact angle and scanning electron microscopy (SEM). The self-cleaning properties of treated fabrics were also analysed based on the photocatalytic ability of coated fabrics. Therefore, the decomposition of methyl orange (MO) and the degradation of red wine and curry spots under the irradiation of a solar simulator were analysed. Thus, the incorporation of TiO_2 particles into the cotton fabric promoted self-cleaning and antibacterial characteristics, but the presence of PCM combined with TiO_2 increases the bioactivity of materials.

1. Introduction

The development of textiles with new finishes is an effective way to modify their behavior by improving specific features through the surface functionalization and the combination of new materials and technologies. Currently, the development of textile finishes using TiO_2 NP has attracted interest due to the possibility of producing textiles with UV protection, photocatalytic and self-cleaning properties, in addition to bacteriostatic properties [1–3]. However, the photocatalytic antibacterial effect is not fully understood. It is known that nanomaterials can inactivate the cellular enzymes and damage the DNA but there are several proposed mechanisms. The TiO_2 NP under irradiation generates extremely reactive oxygen species that, when in contact with the microbial cells, induce an intracellular enzymatic oxidation, which results in a decrease in respiratory activity and consequent death of the cell [3,4]. However, the peroxidation of the polyunsaturated phospholipid components of the membrane [5], or the decomposition of the cell wall and, subsequently, the cell membrane, resulting in a leakage of intracellular molecules [6], are also proposed. On the other hand, there is universal agreement on the effect of reactive oxygen species such as OH*, HO_2* and O_2^-* in the failure of essential functions that depend on the intact membrane structure [3,5].

The development of materials with multiple functionalities is a market imperative that places new challenges on textile processing. The main goal of our study was to prepare, characterize and evaluate self-cleaning, antimicrobial and comfortable cotton fabrics, achieved by a finishing process that combines TiO_2 NP and microcapsules of PCMs.

2. Experimental

2.1. Materials and Process

The samples used were composed of bleached taffeta plain-weave fabrics, 100% cotton, 585 g/m^2, supplied by Têxtil Belém (Brasil). The TiO_2 NP (Aeroxide, P25) were purchased from Quimidroga (Spain), microcapsules of PCMs were supplied by Devan (Portugal), all other reagents were purchased from Sigma-Aldrich (Portugal). The TiO_2 NP (6%) was applied alone or combined with mPCM (300 g/L). The solutions were prepared under constant stirring (900 RPM) at a temperature of 25°C. The application process was performed both in one and two application steps: impregnation with TiO_2 NP, followed by drying and application of mPCM; or application of TiO_2 and mPCM on the same bath. After the impregnation process, the samples were dried at 100ºC during 2 minutes and cured at 140ºC during 2 minutes as well. Finally, they were rinsed thoroughly with tap water and air dried.

2.2. Characterization

2.2.1. Surface characterization

Cotton samples subject to Attenuated total reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) were recorded on Avatar 360 ATR-FTIR spectrophotometer (Madison, USA). Each spectrum was scanned 60 times with a resolution of 16 cm^{-1}. KBr pellets, TiO_2 and NaCl pellets of mPCM were made and analysed in the same equipment without the ATR device. SEM and EDS analysis (NanoSEM, NOVA 200, FEI Co. Oregon, USA) was used to characterize the surface of cotton fabrics before and after treatments with TiO_2 and mPCM, as well as before and after washing. The analyses were performed in high resolution, after coating a thin layer of palladium gold. Static and dynamic contact angle measurements were carried out on a measuring instrument of DataPhysics Instruments (Filderstadt, Germany), with the OCA 20 software. Each sample was measured ten times.

2.2.2. Self-cleaning evaluation

2.2.2.1. Photocatalytic degradation of methyl orange (MO)

The effect of modified samples on the discoloration of a solution of MO was evaluated. Samples (2.5x2.5cm) were placed separately in 50ml of MO solution (4 mg/L). These solutions were shook for 30 minutes in the dark, in order to achieve the adsorption equilibrium [1]. Then, they were exposed to UV radiation (Philips TLD 12W/08 UV lamps, 365 nm; 10cm of incidence distance) maintaining vigorous agitation. The concentration of the solutions was monitored through absorption measurements at 464 nm using a calibration curve (Shimadzu UV-1800 spectrophotometer, Japan).

2.2.2.2. Assessment of Red Wine and Curry Stains degradation

Photocatalytic efficiency of functionalized fabrics (4.5x4.5 cm) was assessed through the degradation of red wine (Casa Ferreirinha, 11.5% alcohol) and curry (5g powder/100mL) stains (2 drops) [2].
The samples were exposed to irradiation (UVA 315 at 400 nm, 0.75 W/m^2/nm) on the QUV Tester (Q-LAB, USA) test instrument. The results were visually analysed by comparing the spectrophotometer reflectance measurements.

2.2.3. DSC analysis

DSC analyses were performed using the differential scanning calorimeter Mettler Toledo DSC-822e instrument (Giessen, Germany). The tests were performed in triplicate, covered random areas of each sample and the average values were recorded. The weight of sample was kept constant (9.4 ± 0.1 mg).

2.2.4. Effect of Washing on Thermoregulation and on the Self-Cleaning Performance

The tests related to the thermoregulation and self-cleaning effect of functionalized cotton fabrics were repeated after the washing process. The washing conditions were defined and performed in accordance with ISO 105-C06:2010, test A15. Samples were evaluated after 1 and 5 washing cycles, comparing the DSC thermograms with the photodegradation of the MO dye.

2.2.5. Test of antimicrobial efficiency
The antimicrobial activity assessment was carried out in accordance with a modified procedure of the AATCC 100:2004 standard method. *Escherichia coli* ATCC® 25922TM, *Staphylococcus aureus* AATCC® 6538TM, and *Candida albicans* ATCC® 10231TM were tested. Samples (6,25cm^2) were sterilized in an autoclave at 121°C for 15 min. Two samples of each condition (cotton, cotton with TiO_2, cotton with TiO_2 and mPCM) were placed in separate Erlenmeyer flasks (100mL), subsequently, 0.5ml of inoculum was added to each jar, containing microorganisms in the range of 0.11-2.8x10^5 colony forming units (CFU)/mL. The number of viable cells was counted manually at 0h, 1h and 4h of UV irradiation (Philips TLD 18W/08 UV lamps, 365 nm), being the results expressed by means of colony forming units CFU/mL, considering the average of the duplicate counts.

3. Results and Discussion

3.1 Characterization of the surface of cotton samples
The surface of the samples was analysed using SEM and EDS. It should be noted the TiO_2 NP (Figure 1b) and the TiO_2 NP with the mPCM (Figure 1c) on the surface of the fabric. Figure 1b confirms a homogeneous distribution of the TiO_2 NP, while Figure 1c shows a formation of some TiO_2 NP aggregated with mPCM relatively dispersed on the surface, a thin layer of coating was formed. Furthermore, EDS results confirmed the presence of TiO_2 nanoparticles and Silane (for applications of TiO_2 and mPCM) on the surface of functionalized cotton.

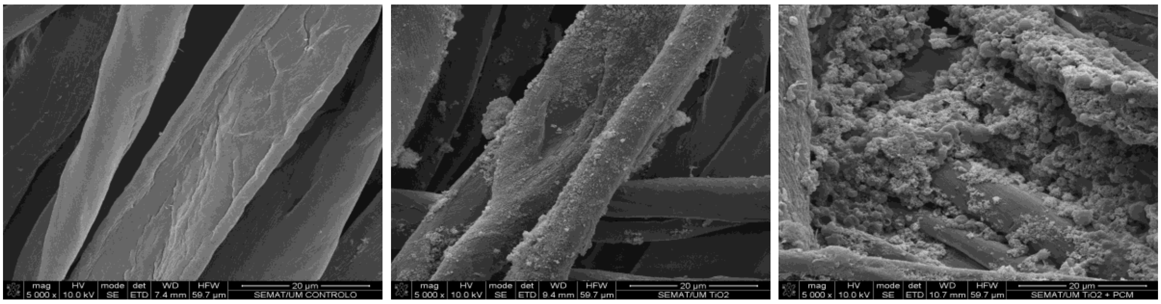

Figure 1. SEM images (a) untreated cotton, (b) cotton with TiO_2 and (c) cotton with TiO_2 and mPCM.

All samples were characterized using IR spectroscopy (results not shown). Cotton spectrum show a broad band in the range 3600-3100cm^{-1}, corresponding to the –OH stretching vibration of cellulose, and the asymmetric stretching of C–H is observed in the ranges 2900cm^{-1} and 1450–1350cm^{-1}. The complex absorption in the 1250-900cm^{-1} range is associated with stretching C-O-C groups of the cellulose [7]. TiO_2 (powder) shows a characteristic peak at 494cm^{-1}, however, when analysing the spectrum of the sample treated by conventional deposition of TiO_2 (region < 700cm^{-1}), the characteristic peak of TiO_2 was not observed, since it is totally dominated by the spectrum of the fiber [8]. It should be noted that cotton with TiO_2 and mPCM has a small peak at 805cm^{-1} related to the breakdown of Si-O-Si groups due to the formation of Si-O-cellulose binding [9]. Also, a low intensity single broad band at 891-912cm^{-1} indicates the SiOH and Si–O–Ti bands overlapped, in agreement with similar applications [3]. Furthermore, the increase in the intensity of the absorption bands related to stretching vibrations of CH at the ranges 2924cm^{-1} and 2854cm^{-1} was observed due to the contribution of paraffin chains of PCM [10]. Further analysis will show that this spectrum also indicates the reaction between -CO-CH = CHR of mPCM with the O-H groups in cellulose [11].

The static and dynamic contact angles were measured to evaluate the wetting properties of modified surfaces. The surface is considered hydrophilic (smaller than 30°) or hydrophobic (higher than 90°) [12]. Concerning the untreated sample and the sample treated with TiO_2 NP, the drops are immediately absorbed. Nevertheless, cotton with TiO_2 and mPCM shows a contact angle of 132.4°. Though, the average time for the absorption of the water drop is of 1.9 seconds approximately, suggesting that the surface is still hydrophilic.

3.2. Photocatalytic degradation of dye

The photocatalytic behavior of the modified materials was evaluated through the degradation effect on MO. The mechanism of organic decomposition is well known, highly oxidative radicals are generated on the surface of TiO_2 [1]. To assess specifically the activity of TiO_2, a previous test was performed using TiO_2 powder (with an amount similar to that estimated to be present in the fabric after the finishing process). The results were compared with those obtained from a finished cotton sample and a control sample. After the exposure to UV, the solution with TiO_2 powder needed approximately 15h to reduce 100% of color, while the solution with a cotton sample reduced 89% of color, and the control solution was decolorized at about 42% (24h).

The samples obtained through the application of TiO_2 and TiO_2 with mPCM in the same bath (1 step) or in sequential baths (2 steps) were compared in terms of photocatalytic behavior after 10h of light exposure. Similar results were obtained from the samples with application of TiO_2 alone or combined by a 2 steps process, with 42.5 and 48.8% of color reduction, respectively [1,2], attributed to the dispersed anatase satisfactorily crystallized on the surface, as opposed to the sample resulting from the application in one step (14.6%). However, the photocatalytic activity of samples functionalized with TiO_2 and mPCM was reduced to similar values after 5 washing cycles, corresponding to 13.7% and 15.7% of MO degradation, respectively (Figure 2). These results agree with those obtained by Carneiro et al. [13], confirming a reduced level of nanoparticles attached on the surface and the loss of NP during washing with the consequent decrease in photocatalytic efficiency.

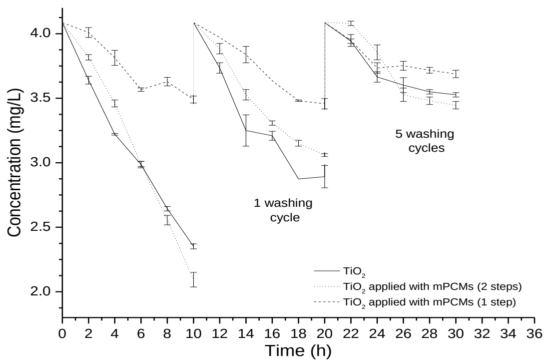

Figure 2. Photocatalytic activity coated cotton

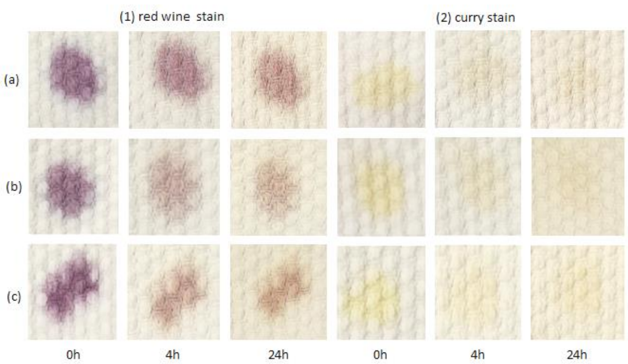

Figure 3. Degradation of stains in a (a) cotton control, (b) cotton with TiO_2 and (c) cotton with TiO_2 and mPCM after exposure to light irradiation.

3.3. DSC analysis

DSC analysis was performed to determine the thermal behavior of the prepared samples. The calorimetric results depend directly on the amount of mPCM fixed in the surface, but it is also related to other factors, like the textile structure [14,15]. Based on a gravimetric analysis, the amount of mPCM on fabric was 8.7 ± 2.4% (w/w) when applied alone and 9.58 ± 1.9% (w/w) when applied with TiO_2. Despite this slight difference in NP content, the thermograms showed differences concerning the latent heat storage between the samples. While samples with mPCM showed 5.86 ± 0.3 J/g, the samples with mPCM and TiO_2 presented 2.56 ± 0.07 J/g. Moreover, both samples showed a slight difference in latent heat storage even after 5 cycles of washing fastness, 4.31 ± 0.21 J/g and 1.41 ± 0.11 J/g, confirming the integrity of microcapsules added into the textile. Similar results were presented by Karthikeyan et al. and Shin et al. [16,17].

3.4. Assessment of Degradation Activities of Red Wine and Curry Stains

Figure 3 presents the results concerning the degradation of red wine and curry stains in control samples, cotton with TiO_2 and cotton treated with TiO_2 and mPCM, before and after light irradiation in QUV Tester equipment. The stains in the cotton treated with TiO_2 (b) and in the cotton treated with TiO_2 and mPCM (c) present a slight difference in color. However, cotton control (a) exhibited a lower level of discoloration. This indicates that the fabrics coated with TiO_2 have an increased performance in stain degradation activity, in agreement with the results obtained in the degradation of MO (Figure 2). Nevertheless, even after 24 hours of exposure to light, there was no complete discoloration of the wine stain in the samples. On the other hand, curry stain was completely decolorized, independently of the TiO_2 coating sample. Furthermore, it is perceptible, after 4h of light irradiation, a yellowing of the samples. It indicates that TiO_2 layers on substrates can assist in discoloration stains, but are harmful after prolonged light irradiation.

3.5. Assessment of antimicrobial efficiency

The photocatalytic evaluation of the antimicrobial activity of cotton fabrics treated with TiO_2 and TiO_2 with mPCM was determined as described above. UV irradiation had no significant effect on bacteria number in the untreated samples. Samples with different finishes presented similar results and, when compared with the control, there was a reduction of cell number, more expressive after longer UV exposure (4h). For *S. aureus,* the sample treated with TiO_2 showed a reduction of 37% and the sample treated with TiO_2 and mPCM a reduction of 98%. For *E. coli*, the sample treated with TiO_2 presented a reduction of 2.5% and the sample treated with TiO_2 combined with mPCM a reduction of 58%. However, the observed efficiency was lower when compared with that described in other studies [3,18,19]. Maness et al. [5] reported a complete reduction of microorganisms and found that a low dose of TiO_2 (0.1 mg/mL) in the presence of UV light was able to kill *E. coli* cells with an initial cell concentration of less than 10^5 CFU/mL but failed to efficiently kill the cells at the concentration of 10^8 CFU/ml. Nevertheless, our results are encouraging since the concentration of microorganisms tested was 0.11-2.8x10^5. For the yeast, *C. albicans*, the sample treated with TiO_2 showed a reduction of 73%, but the control samples presented a similar result (77%), in opposition to the samples treated with TiO_2 and mPCM, with 27.5%. According to Abu et al. [20], *C. albicans* can suffer a drastic reduction in the number of cells if exposed to UV radiation, influenced by the intensity of the radiation or the time of exposure. In addition, it is important to note a slight decrease in the adhesive properties of the material treated with TiO_2 and mPCM, which could influence antimicrobial behavior [21].

4. Conclusion

In this study, a cotton fabric with thermoregulation and antibacterial action against *S. aureus* and *E. coli* was obtained through the application of TiO_2 NP and mPCM. One step and two steps finishing processes were analysed and the results showed that the best application process in terms of self-cleaning activity and thermoregulation properties was obtained with the two steps finishing process. Furthermore, the antibacterial effect was increased by the presence of mPCM.

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