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Preparation and characterization of cotton fabrics with antimicrobial properties through the application of chitosan/silver-zeolite film

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Abstract

The development of antimicrobial cotton fabrics using chitosan/silver-zeolite film has been investigated in the present work. The film was applied to 100% cotton fabric using a common pad-dry-cure technique and citric acid was used as crosslinking agent. The resulting fabrics were characterized through infrared spectroscopy (FTIR), contact angle and scanning electron microscopy with X-ray microanalysis (SEM/EDS). The antimicrobial activity of the fabrics was assessed through the viable-cell counting method and the materials showed activity against *S. aureus* and *T. rubrum.* The textile performance of the fabrics was analysed regarding their characteristics of hydrophilicity and breathability. The finishing did not change the hydrophilic behaviour of the material. Although the permeability to air has reduced 20%, the permeability to water vapour remained practically unchanged. Therefore, the results suggested that the process approach of applying chitosan/silver-zeolite film is recommended to produce textiles with antibacterial properties.

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Keywords: Cotton finishing, antifungal; antibacterial, chitosam/silver-zeolites film

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1. Introduction

Textile materials, especially those of natural origin, have long been recognized as being environments susceptible to microbial proliferation. They enable the development of fungi and bacteria as they act, for these microorganisms, as sources of energy or of nutrient retention due to their molecular structure. Besides, they provide hot and humid environments, which are ideal for their proliferation. Synthetic fibres are more resistant to the microbial attack because they are hydrophobic. However, regardless of their origin, most fibrous materials allow the propagation of microorganisms [1–3].

The problem of microbial proliferation also directly affects users of textile products, since microorganisms can cause bad odours, skin irritations and even, in some cases, infections. Given the need to protect textile materials from undesirable aesthetic changes and to prevent problems related to the hygiene and health of the user, the production of textile materials with antimicrobial finishes has increased over the last years [2,4,5]. Antimicrobial textiles are used in the production of the most diverse types of products, from simple decorative articles to technical textiles, from sportswear and protective clothing to articles for medical application [6,7].

The metal salts and the particles with metals have been applied in the industry to give the materials antimicrobial properties. The evaluation of the antimicrobial performance of these compounds has been widely studied since they exhibit activity even at very low concentrations [8]. In industrial applications, the emphasis is on those compounds in the form of nanoparticles since they possess a high specific surface area, which allows an increase in the concentration of retained metal atoms, intensifying the antimicrobial activity [9].

Among the materials that release silver ions are included silver zirconium phosphates and zeolites with silver [10]. In this case, the materials used as matrix have a morphology and size distribution that can be in the range of microns, and, in this case, cannot be defined as nanomaterials [11]. They act through the release of silver ions when in contact with the fluids, for example, found in a wound. They bind to the disulfide (-S-S-) and sulfhydryl (-SH) groups of the cell wall proteins, causing an interruption of the metabolic processes, inhibiting growth and causing the death of the cells.

The effects caused by the accumulation of silver, both in humans and in other living species, are known and worrying, therefore, significant efforts have been made by the industry in the search for new antimicrobial products that minimize the amount of silver used without impairing the intended effect [8,12].

Natural zeolites are porous crystalline materials of hydrated sodium aluminosilicate. They have a permanent negative charge that can be equilibrated by interchangeable cations, which justifies their use as adsorbent, cation exchanger and catalyst for multiple uses. These unique characteristics allow their application aiming to, simultaneously, increase the antimicrobial, anti-UV or flame retardant properties of the materials [13–15].

Zeolites have a strong affinity for Ag^+, binding to this ion electrostatically up to, approximately, 40% (w/w) within its framework. Therefore, silver-zeolites can provide finishes with antibacterial properties. The application of SZ, dispersed in a polycarboxylic acid solution, to cellulosic materials may be an interesting possibility to produce antimicrobial textile fabrics, for use in various health and well-being areas [15,16].

Among the natural polymers, chitosan has attracted much attention due to its unique combination of properties. Being biodegradable and biocompatible, its antimicrobial properties have been explored for a variety of applications in the most diverse areas. More recently, its ability to coordinate with metal ions, forming complexes, has been used to improve its bioactivity [17–21].

This work focused on the preparation and characterization of cotton finished with chitosan/silver zeolites film and on the evaluation of its antimicrobial activity.

2. "Material and methods"

The samples used were composed of bleached taffeta plain-weave fabrics, 100% cotton, 585 g/m^2, supplied by Têxtil Belém (Brazil). The Chitosan (Chitoclear® 42030) was purchased from Primex (Iceland), zeolites 4A (LTA) doped with silver ≈0.3% (w/w) were offered by the Department of Physics of the School of Engineering of the University of Minho, all other reagents were purchased from Sigma-Aldrich (Portugal).

The Chitosan (0,2% w/w) was dissolved in 1% (v/v) of acetic acid under constant stirring (900 RPM) during 4h at a temperature of 50°C. The solution with chitosan was mixed with SZ (2,5g/L) under constant stirring (1100 RPM) at a temperature of 25°C during 10 minutes. Just before application, the citric acid (80g/L) and catalyst was added to the finishing formulation. The cotton samples (5.0 X 5.0cm; 0,95±0.1g) were impregnated (pick-up 90%), dried at 90ºC during 3 minutes and cured at 160ºC during 2 minutes. Finally, they were rinsed thoroughly with tap water and air dried [22].

Fourier Transform Infrared spectroscopy (ATR-FTIR) analysis of cotton samples were carried out on Avatar 360 ATR-FTIR spectrophotometer (Madison, USA). Each spectrum was recorded within the range of 400-4000 cm^{-1} and scanned 60 times with a resolution of 16 cm^{-1}.

SEM and EDS analysis (NanoSEM, NOVA 200, FEI Co. Oregon, USA) was used to characterize the surface of cotton fabrics before and after treatments. The analyses were performed in high resolution, after coating with a thin layer of palladium.

Static contact angle measurements were carried out in the OCA 20, of DataPhysics Instruments (Filderstadt, Germany). Each sample was measured ten times.

The air permeability was measured with the Textest FX 3300 equipment, in accordance with ISO 9237:1995 standard method. All tests were performed at the same pressure (100 PA). The water vapor permeability test was carried out in a Labthink TSY-W1 Water Vapor Permeability Tester in accordance with BS 7209:1990 standard method.

The antimicrobial activity assessment was carried out in accordance with a modified procedure of the AATCC 100:2012 standard method. *Escherichia coli* ATCC® 25922™, *Staphylococcus aureus* ATCC® 6538™, *Candida albicans* ATCC® 10231™ and *Trichophyton rubrum* (a clinical isolate from skin dermatophytosis-FF9) were tested. The samples (6,25cm2) were sterilized in an autoclave at 121°C for 15 min. The number of viable cells was counted manually at 0h and after 20h, being the results expressed by means of colony forming units CFU/mL, considering the average of the duplicate counts.

3. Results

The morphology of the surface of the samples coated with chitosan/silver zeolite film and cross-linked with citric acid was analysed. The micrographs of treated cotton fabrics, obtained through SEM, are presented in Figures 1a and 1b. The diameter of the silver zeolites is, for the most part, within the sizes in the range 0,5-3,5 µm. The images show zeolites distributed in the surface and, also, fixed in the fibre spacing due to the esterification reaction with the chitosan film. Furthermore, it is possible to observe an agglomeration of zeolites in the film and the adhesion of these composites into the cotton fibres. Similar behaviour was described by Wang et al. [23] about preparations of chitosan with zeolites with diameters between 3 and 5 µm.

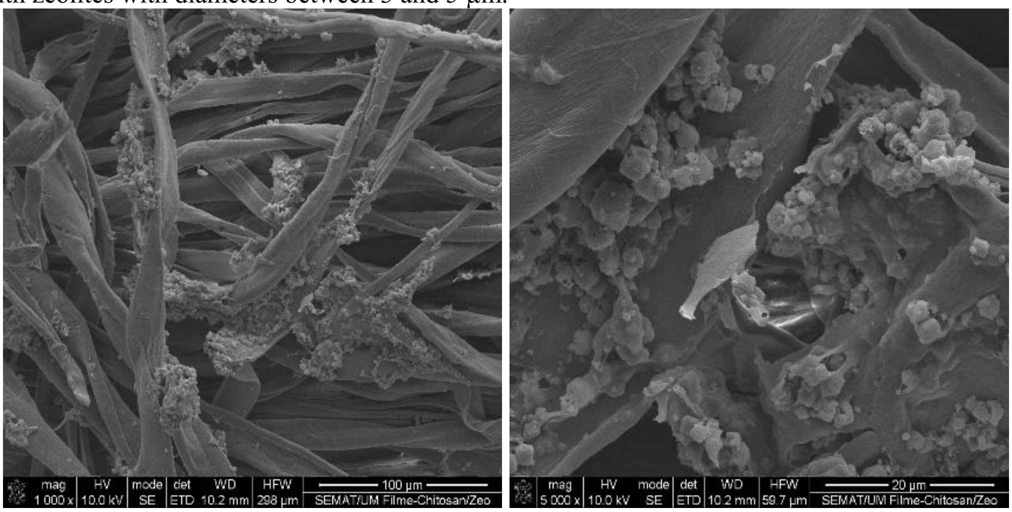

Fig. 1. SEM micrograph (a) 1000x magnification, (b) 5000x magnification.

In agreement with the micrographs, the EDS (Fig. 2) analysis confirms the presence of chitosan and zeolites in the surface of cotton through the presence of the common elements of zeolites, Al and Si. The Mg and Cl peaks, related to the catalyst, are also identified. In fact, based on a gravimetric analysis, the cotton was coated with 8.62 ± 0.39% (w/w) of chitosan/silver zeolites film.

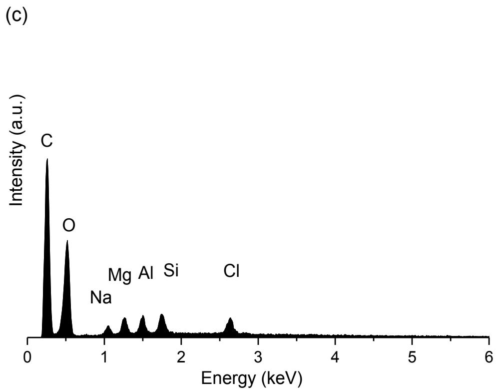

Fig. 2. EDS analysis of cotton treated with chitosan zeolite film.

The samples were characterized with resource to FTIR-ATR. Figure 3 shows spectra of cotton (control) and cotton with chitosan/silver zeolite film (CS-SZ film). The broad band in the range 3330-3260cm^{-1}corresponds to the –OH stretching vibration of cellulose, and the asymmetric C–H stretching is observed in the range 2900cm^{-1}. The complex absorption in the range 1250-900cm^{-1} is associated with C-O-C stretching groups of cellulose.

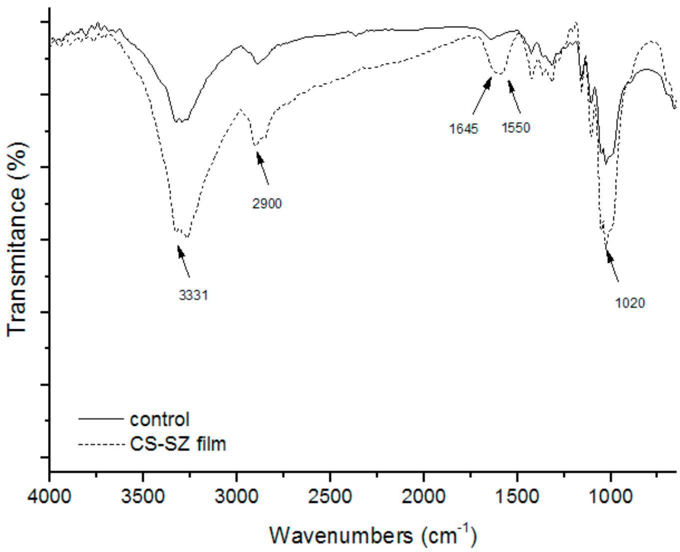

Fig. 3. FTIR spectra of cotton treated with film of chitosan and zeolites.

The peak in the range 1550-1645cm^{-1}, which can be attributed to the film of chitosan/silver zeolite, confirmed that the cotton was grafted successfully. The new peak at 1645cm^{-1} (C=0 stretching) and the extension at 1550cm^{-1} resulting from possible -NH bending vibration of the amine groups indicate that the chemical reaction occurred between chitosan and COOH groups of citric acid [22].

The contact angle (Fig. 4) was measured to evaluate the wetting properties of modified surfaces. The surface is considered hydrophilic (smaller than 30°) or hydrophobic (higher than 90°) [24]. Concerning the untreated sample and the sample treated, the drops are immediately absorbed, confirming that the surface is still hydrophilic.

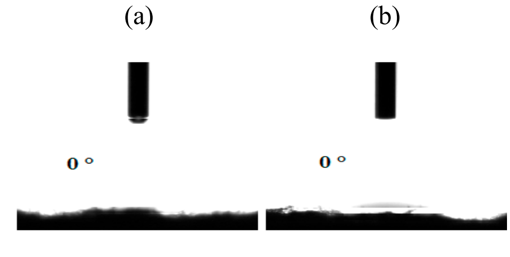

Fig. 4. Static contact angle of samples treated with film of chitosan and zeolites.

The functionalized material maintained acceptable properties in terms of breathability. The permeability to water vapour was almost the same of the untreated cotton (decreased only 3%) and the permeability to air decreased about 20%, less than the 30% described by other researchers for similar coatings [21].

The activity of the cotton and the cotton with chitosan/silver zeolites film was tested against gram-positive and gram-negative bacteria, yeasts and fungi. Considering the results obtained (table 1), the cotton functionalized with chitosan/silver zeolites showed selective antimicrobial activity. It was active against *S. aureus* and *T. rubrum* but inactive against *E. coli* and *C. albicans.* It is well-known that chitosan itself has antimicrobial activity due to its cationic amino groups, that is to say, positively charged chitosan can bind to the surface of the bacterial cell, which is negatively charged, and disrupt the normal functions of the membrane [18,20]. However, the antimicrobial activity of the chitosan films can change in different ways, depending on several factors, such as the composition of the films, the weight-average, the viscosity and the degree of deacetylation of the chitosan, in addition to environmental conditions, especially, pH [25–28].

Rhim et al. [29] reported that chitosan-based films with silver nanoparticles and Ag-zeolite (2,1-2,8 wt% of silver) exhibited antimicrobial activity against the two gram-positive bacteria, *S. aureus* and *L. monocytogenes*, and the two gram-negative bacteria, *S. typhimurium* and *E. coli*, while no activity was noted on chitosan films. In our work, the concentration of zeolites in the film is 2 to 10 times lower and the relative amount of silver included is, at least, 20 times lower [29]. This difference could justify the disparity in the antimicrobial behaviour. However, it should not be forgotten that the mechanism of the antimicrobial action of chitosan and its derivatives is not a simple or a fully understood mechanism, but an intricated process, not always easy to explain [28,30].

Table 1. Reduction of microorganisms (%) in textile samples

Sample	*E. coli*	*S. aureus*	*C. albicans*	*T. rubrum*
Control Sample	[a]	[a]	[a]	[a]
Cotton with chitosan/ silver zeolites film	[a]	99 ± 0.7	[a]	83.3 ± 2.2

[a] no inhibition

Conclusion

In this study, a cotton fabric with antibacterial action against *S. aureus and T. rubrum* was produced and characterized. The finishing process involved the application of chitosan/silver zeolites film. The resulting material retained the hydrophilic behaviour and the water vapour permeability. The air permeability has decreased, but at a level that does not compromise its textile application.

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