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DEVELOPMENT OF A PLASMA ACTIVATED MULTIFUNCTIONAL POLYESTER FABRIC USING ZINC OXIDE NANOPARTICLES AND CITRONELLA OIL MICROCAPSULES

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ABSTRACT

There is a high demand for the development of textiles possessing multifunctional properties for outdoor, protective and health care applications. The coating of polyester (PES) textiles with metal nanoparticles and essential oils may act in a synergistic mode to obtain materials with improved antimicrobial and UV-protection properties. However, the lack of functional groups onto PES structure makes the adhesion of particles a difficult task. In this work, PES fabric was activated by dielectric barrier discharge (DBD) plasma treatment, and functionalized with zinc oxide nanoparticles (ZnO NPs) and poly (methyl methacrylate) (PMMA)-citronella microcapsules by dip-coating.

KEYWORDS

UV-protective textiles, antimicrobial textiles, microcapsules, nanoparticles

INTRODUCTION

Antibacterial, anti-fungal, self-cleaning, UV protection, and hydrophilic properties have made metals and metal oxides important active agents for advanced textiles [1]. Incorporating the metals and metallic oxides on the nanoscale into the textile substrates can introduce the aforementioned functionalities which are not inherent in the textile substrates. Among many metal nanoparticles (NPs), Zinc Oxide (ZnO) NPs are promising due to their optical, antibacterial, magnetic, self-cleaning, antibacterial, and semiconducting properties [2]. ZnO NPs display excellent antibacterial properties and non-toxicity towards human cells. Thus, ZnO NPs have been incorporated in several protective materials [3-5]. The microencapsulation of essential oils has been used as a suitable strategy for the development of effective release models. Citronella oil is a biopesticide with a non-toxic mode of action and antimicrobial properties [6-7]. Poly (methyl methacrylate) (PMMA) is a potential material to produce microcapsules due to its non-toxic nature, good mechanical properties and easy processing [8-9]. Therefore, the functionalization of polyester fabric with ZnO NPs and citronella microcapsules (MCs) can promote multifunctional properties. The application of these both agents have shown interesting synergistic properties [10]. Coating techniques are used to create functional textiles [4]. However, poor adsorption of ZnO NPs to the textiles is a limitation. The addition of binding agents or changing the chemistry of the substrate are some of the methods to improve the adsorption. An eco-friendly technique such as dielectric barrier discharge (DBD) plasma treatment can be used to modify the surface properties of the fabrics by introducing new functional groups and active species to increase the adsorption of ZnO NPs



onto the textiles [5]. Adsorption may be enhanced due to hydrogen bonds, van der Waals or dipolar interactions [11].

In this study, DBD plasma treated and untreated PES fabric was coated with ZnO NPs and citronella-PMMA microcapsules. The UV-protective properties and antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli* of the samples were tested.

MATERIALS AND METHODS

1. Materials

Plain weave commercial PES fabric with a weight per unit area of 100 g.m⁻² was washed prior to use by applying 1.0 g.L⁻¹ of a non-ionic detergent at 60 °C for 30 min with a liquor ratio of 1:100, rinsed with distilled water and dried at 40 °C. ZnO NPs (<50 nm) were acquired from Merck.

2. Citronella microcapsules synthesis

The PMMA microcapsules (MCs) were synthesized according to Al-Nemrawi et al.[12], with a concentration adjustment of 3 wt.% SDS and 5 wt% PVA, and by adding Citronella oil.

3. Atmospheric DBD Plasma in air

DBD plasma treatment was performed in a semi-industrial prototype (Softal GmbH/University of Minho) according to the conditions described by Mehravani et al. [11]. The dosage applied onto PES fabric was 7.5 kW m².min⁻¹.

4. Dispersions and PES samples preparation

ZnO NPs water dispersion (2 mg.mL⁻¹) using polyethyleneimine as stabilizing agent (0.01%(w/v)) was prepared in ultrasonic bath for 15 min followed by ultrasonic treatment for an additional 15 min. Then, sodium dodecyl sulphate (0.05% (w/v)) and citronella microcapsules (0.5% (w/v)) were added to the dispersion. PES (100 cm²) was functionalized by dip coating for 20 min and then dried at 40 °C. Controls of the formulations were prepared, with and without DBD plasma treatment

5. Measurement of UPF

The Ultraviolet Protection Factor (UPF) was determined according to EN 13758-d using UV-Vis Spectrophotometer (UV-2600 -SHIMADZU).

6. Antibacterial evaluation

The antibacterial activity was assessed through an adaptation of American Association of Textile Chemists and Colorists (AATCC) 100 TM 100 as described in Padrão et al. [13]. The tested bacteria were *S. aureus* American Type Culture Collection (ATCC) 6538 and *E. coli* ATCC 25922.

RESULTS AND DISCUSSION

PES fabric was successfully functionalized with ZnO NPs and citronella oil MCs. Microscopic images showed the presence of MCs in all samples with a good distribution (Figure 1). The UPF values were calculated and all samples showed similar or superior protection compared with control samples. In the samples functionalized with both ZnO NPs and MCs, the best result was obtained when DBD plasma treatment was performed (Table 1). The differences may be attributed to the amount, distribution and agglomeration state of ZnO NPs in the samples. The values were highest for the PES with only MCs. Control samples display excellent UPF values, however in the majority of the conditions the ZnO NPs and MCs further enhanced UPF due to light reflection and scattering.

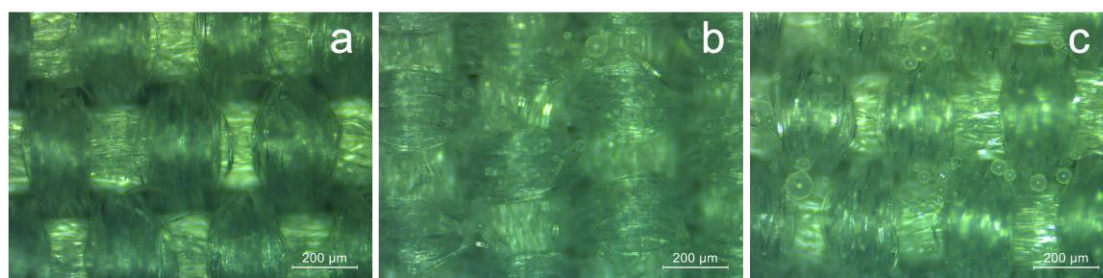


Figure 1. Images of the samples containing ZnO NPs and MCs at a magnification of 100x. a) PES b) PES+ZnO+MCs c) PES DBD+ZnO+MCs (images obtained by a Leica DM750 microscope and a Leica MC170 HD camera).

Table 1. UV-Protection of the PES samples.

SAMPLES	UV-A	UV-B	UPF
PES	12.2	0.6	57
PES DBD	12.2	0.6	57
PES + ZnO	11.6	0.6	60
PES DBD + ZnO	11.7	0.6	56
PES + MCs	10.3	0.4	71
PES DBD + MCs	10.1	0.5	71
PES+ZnO + MCs	13.5	0.6	52
PES DBD+ZnO+MCs	10.8	0.5	63

Figure 2 displays the antibacterial properties of the PES samples. Interestingly, all formulations exhibited a high effectiveness against *S. aureus*, where the samples PES + MCs or PES + ZnO + MCs with and without DBD showed disinfection properties. Whereas, against *E. coli* all samples exhibited low or moderate antibacterial activity. However, the PES + ZnO + MCs, with and without DBD, exhibited a reduction of 99.99999 % (log reduction >6), indicating an effective sterilization [14]. The synergistic effect against *E. coli* was evidenced by comparing the antimicrobial results of the sample only with MCs or ZnO NPs, where a low antimicrobial effect was found comparing with the samples with both ZnO NPs and MCs. In the sample with both MCs and ZnO NPs, the antimicrobial results increased to log reduction of 7. The results were in accordance with the literature, where better properties of citronella MCs against *S. aureus* and superior properties of ZnO NPs against *E. coli* were found [15]. Thus, it can be concluded that the combination of MCs of citronella oil and ZnO NPs have the potential to be used in biomedical applications to fight against *S. aureus* and *E. coli*.

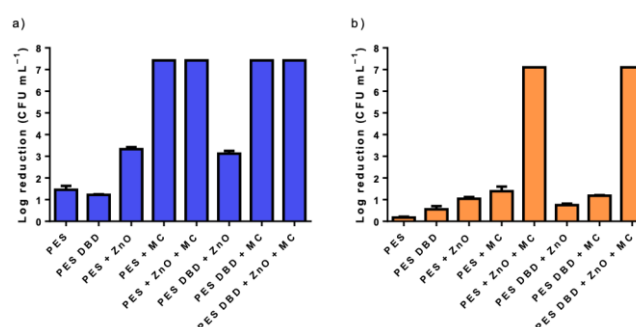


Figure 2. Antibacterial activity evaluation against: a) *S. aureus* and b) *E. coli*.

CONCLUSION

DBD plasma treated PES fabric functionalized with ZnO NPs and citronella microcapsules showed to increase the UPF of the fabric and also acting in synergy according to antimicrobial results. Furthermore, due to the presence of citronella, the developed textile displays potential insect replant properties. Therefore, the developed fabric present potential to be used in outdoor, protective and health care textiles. These may encompass the development of hospital tents.

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REFERENCES

- [1] Amani A., Montazer M., Mahmoudirad M., *Synthesis of applicable hydrogel corn silk/ZnO nanocomposites on polyester fabric with antimicrobial properties and low cytotoxicity*, International Journal of Biological Macromolecules 2019, vol. 123, pp. 1079-1090.
- [2] Munir M.U., Ashraf M., Abid H.A., Javid A., Khanzada H., *Coating of modified ZnO nanoparticles on cotton fabrics for enhanced functional characteristics*, Journal of Coatings Technology and Research 2021, vol.19, pp. 467-475.
- [3] Martinaga Pintarić, L., Somogi Škoc, M., Ljoljić Bilić, V., Pokrovac, Rezić I., *Synthesis, Modification and Characterization of Antimicrobial Textile Surface Containing ZnO Nanoparticles*, Polymers 2020, no 12.
- [4] Verbič A., Gorjanc M., Simončič B., *Zinc Oxide for Functional Textile Coatings: Recent Advances*, Coatings 2019, no 9.
- [5] Jazbec K., Šala M., Mozetič M., Vesel A., Gorjanc M., *Functionalization of Cellulose Fibres with Oxygen Plasma and ZnO Nanoparticles for Achieving UV Protective Properties*, Journal of Nanomaterials 2015, pp. 1-9.
- [6] Bezerra F.M., Lis M., Carmona Ó.G., Moraes F.F., *Assessment of the delivery of citronella oil from microcapsules supported on wool fabrics*, Powder Technology 2019, vol. 343, pp. 775-782.
- [7] Koşarsoy Ağçeli G., Hammamchi H., Cihangir N., *Novel levan/bentonite/essential oil films: characterization and antimicrobial activity*, Journal of Food Science and Technology 2021, vol. 59, pp. 249-256.
- [8] Bisht A., Kumar V., Maity P.C., Lahiri I., Lahiri D., *Strong and transparent PMMA sheet reinforced with amine functionalized BN nanoflakes for UV-shielding application*, Composites Part B: Engineering 2019, vol.176.
- [9] Feuser P.E., Gaspar P.C., Ricci-Júnior E., Silva d. M.C.S., Nele M., Sayer C., de Araújo H.H. P., *Synthesis and Characterization of Poly(Methyl Methacrylate) PMMA and Evaluation of Cytotoxicity for Biomedical Application*, Macromolecular Symposia, 2014, vol. 343, pp. 65-69.
- [10] Motelica L., Ficaí D., Oprea O., Ficaí A., Trusca, Holban A.M., *Biodegradable Alginate Films with ZnO Nanoparticles and Citronella Essential Oil—A Novel Antimicrobial Structure*, Pharmaceutics 2021, vol.13.
- [11] Mehravani B., Ribeiro A.I., Cvelbar U., Padrão J., Zille A., *In Situ Synthesis of Copper Nanoparticles on Dielectric Barrier Discharge Plasma-Treated Polyester Fabrics at Different Reaction pHs*. ACS Applied Polymer Materials, 2022.
- [12] Al-Nemrawi N.K., Marques J., Tavares C.J., Oweis R.J., Al-Fandi M.G., *Synthesis and Characterization of photocatalytic polyurethane and poly(methyl methacrylate) microcapsules for the controlled release of methotrexate*, Drug Development and Industrial Pharmacy 2018, vol. 44.
- [13] Padrão J., Nicolau T., Felgueiras H.P., Calçada., Zille A., *Development of an Ultraviolet-C Irradiation Room in a Public Portuguese Hospital for Safe Re-Utilization of Personal Protective Respirators*, International Journal of Environmental Research and Public Health 2022, vol. 19.
- [14] Nicolau T., Gomes Filho N., Padrão J., Zille A., *A Comprehensive Analysis of the UVC LEDs' Applications and Decontamination Capability*, Materials 2022, vol. 15.
- [15] Motelica L., Ficaí D., Andronescu, E., *Innovative Antimicrobial Chitosan/ZnO/Ag NPs/Citronella Essential Oil Nanocomposite-Potential Coating for Grapes*, Foods 2020, no 9.