AUTEX 2022 Conference Proceedings 978-83-66741-75-1

DOI: 10.34658/9788366741751.129

ANTIVIRAL PROPERTIES OF FLAME RETARDANT BACTERIAL NANOCELLULOSE MODIFIED WITH MORDENITE

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ABSTRACT

Current COVID-19 pandemic has underscored the requirement of antiviral properties in a plethora of textile applications. These include textiles used in home areas prone to fire such as kitchens, windows and electronic panel areas, but also in the automotive industry such interior textiles and hood insulation pad covers. Therefore, this work describes the characterization of a fully sustainable textile: bacterial nanocellulose, functionalized to achieve an impressive flame retardancy.

KEYWORDS

Bacterial nanocellulose, mordenite, zeolite, flame retardant.

INTRODUCTION

Textiles are present in our daily life in varied applications including home textiles, automotive, and clothing. For this reason, flame retardancy of textiles is ubiquitously relevant, and their requirements are described in a series of existing regulations [1]. Cellulosic materials are not inherently ignition resistant thus requiring a flame retardant finishing system treatment to prevent small flame ignition. Among the many industrially important zeolites, mordenite is found to be interesting because of its unique and exceptional physical and chemical properties [1]. Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents and catalysts. Mordenite (MOR) is one of the 234 zeolites with different structures already identified and one of the six most abundant zeolites. Synthesized by the hydrothermal method, MOR is a high-silica molecular sieve possessing two pore channels with an ideal composition of $Na_8Al_8Si_{40}O_{96}.nH_2O$. It is and has been effectively used in the adsorption and separation of gas or liquid mixtures involving acidic components. As a catalyst, mordenite zeolite is used in various important industrial reactions like hydrocracking, hydro-isomerization, and alkylation [2]. The envisaged objective is to reduce the flammability of nonwoven textiles, namely a biopolymer-based textile, bacterial nanocellulose (BNC). BNC is synthesized by bacteria and is composed of a 3D matrix of 100 % nanofibrils of cellulose, each with a diameter ranging between 20 to 100 nm, resulting in a nanoporous mesh with diameter between 100 to 300 nm [3]. When BNC producing bacterium are cultured in static culture, the BNC is formed as membrane at the surface of the culture medium and adopts the shape of the available surface. Therefore, it is easy to control the membrane surface shape, as well as its thickness, which can be controlled by the incubation time (longer incubation time will result in a larger thickness). Such conditions result in a membrane with exhibits mechanical properties roughly equivalent to Kevlar® and an impressive biocompatibility [4]. Therefore, possible applications of this mordenite modified BNC (BNC_MOR) include textiles for curtains in hospital environments, home areas prone to fire such as kitchens, windows and electronic panel areas, but also in the automotive industry such interior textiles and hood insulation pad covers.

MATERIALS AND METHODS

Bacterial Nanocellulose Processing - BNC membranes were obtained from *Gluconacetobacter hansenii* (*G. hansenii*) ATCC 53582 bacteria cultured in a Hestrin and Shramm (HS) culture medium. HS was prepared with 20 g/L glucose (Carlo Erba, Barcelona, Spain), 5 g/L peptone (Himedia, Mumbai, India), 5 g/L yeast extract (Sigma-Aldrich), 2.5 g/L magnesium sulfate (Panreac AppliChem, Barcelona, Spain), 2.7 g/L sodium phosphate anhydrous (Panreac AppliChem), and 1.15 g/L citric acid monohydrate (Merck). The media was prepared in distilled water (dH2O) and autoclaved at 121 °C for 20 min. BNC was obtained by fermenting *G. hansenii* under static culture conditions using HS culture medium at 28 °C. Afterwards, to disrupt the *G. hansenii* cells, the membranes were autoclaved. After cooling, the membranes were rinsed with tap water and submerged into 1 M sodium hydroxide for 24 h to remove any medium residues and cellular debris. The BNC membranes were abundantly rinsed with water until neutral pH is achieved. Finally, the never-dried BNC membranes were cut into 1 mm thick films, autoclaved in dH_2O and stored in aseptic conditions until further use [5].

Mordenite - Mordenite HCZM 40 was obtained from Clariant International Ltd.

Exhaustion method - Previously dried BNC membranes (room temperature) were immersed in a dispersion containing 25 g/L of mordenite in water. For control, BNC membranes were immersed in 60 mL of distilled water. The samples were placed inside IBELUS (C-720, Pregitzer & Ca. Lda.) and left for 8 hours at 60 °C (2 °C/min) under rotation at 50 rpm with cycles of 50 seconds.

Antimicrobial activity - To assess antibacterial effectiveness of mordenite when embedded within a BNC membrane, *Staphylococcus aureus* (*S. aureus* ATCC 6538) and *Escherichia coli* (*E. coli* ATCC 25922) were tested. Trypticase soy broth (TSB) and trypticase soy agar (TSA) media were purchased from Merck. Antiviral assays were performed using MS2 bacteriophage (ATCC 15597-B1) and *E. coli* ATCC 15597 was used as MS2 host. Culture media and conditions used followed the same procedure as described in [6].

Contact inactivation - Bacteria inoculums were prepared in TSB and incubated overnight at 37 °C and 120 rpm. Each test was carried out using an initial concentration of 1.0×10^7 CFUs/mL for the bacteria and 1.0×10^7 PFUs/mL for the virus. BNC_MOR membranes were evaluated quantitatively following an adaptation of the standard AATCC 100-TM100 [6].

Flame retardancy properties - Burn time was verified according to the Standard for the Flammability of Clothing Textiles 16 CFR Part 1610. According to the standard, the test was performed at an angle of 45° and the specimen size was 50 mm by 150 mm. Flammability was measured as the time needed for the sample to completely burn.

Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy - The surface chemistry and chemical composition of the BNC and BNC-NZ films were analyzed by ATR-FTIR. A Shimadzu IRAffinity-1S FTIR spectrophotometer (Switzerland), coupled with a HATR 10 accessory with a diamond crystal, was used to record the films spectra, performing a total of 45 scans at a spectral resolution of 8 cm^{-1}, over a range 400–4000 cm^{-1}. BNC films were air-dried overnight at RT. The samples were placed onto the crystal using air at 20 °C as background.

RESULTS AND DISCUSSION

Following exhaustion, the BNC and BNC_MOR samples were left to dry at room temperature. As observed Figure 1, when mordenite is incorporated in BNC no considerable differences are observed, the BNC_MOR just became slightly darker. Thus, the aesthetical properties were not drastically affected.

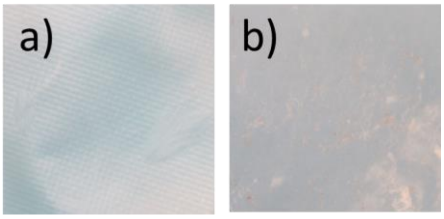

Figure 1. Dry BNC membranes after exhaustion: BNC control (left) and BNC in a 25 g/L dispersion of mordenite in distilled water.

Morphological Characterization – FTIR

BNC_MOR samples exhibit characteristic absorbance bands of pristine BNC, hydroxyl stretching vibration (3353 cm^{-1}) and aldehyde stretching (2916 cm^{-1}) [5]. Mordenite zeolite presents a strong T–O stretching vibration band (~ 1057–1070 cm^{-1}), where T is commonly silicon and aluminum. Other bands appear near 787 cm^{-1} (amorphous SiO_2), 555 cm^{-1} (feldspar) and 400 cm^{-1} (Si-O-Si bending vibration) [7]. BNC_MOR presents typical pristine BNC (3353 cm^{-1} and 2916 cm^{-1}). Although faintly perceivable, BNC_MOR does not seem to present typical MOR characteristic peaks which could be due to a smaller concentration compared to BNC or by being masked by the BNC band.

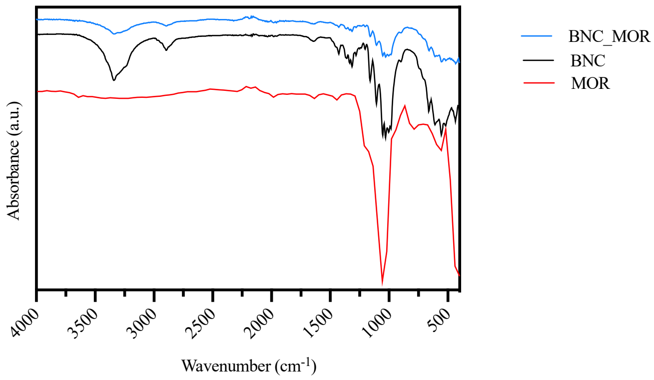

Figure 2. ATR-FTIR spectra BNC_MOR and BNC films, and MOR (4000–400 cm^{-1}).

Antimicrobial activity

The antimicrobial efficacy of the MOR modified BNC was assessed using bacteria *E. coli* and *S. aureus* and MS2 bacteriophage by contact inactivation. BNC without functionalization was used as control and as expected, showed no relevant antimicrobial effect. BNC_MOR did not present bacterial reduction for *E. coli*, contrary to what has been suggested in the literature [8]. On the contrary, a maximum of 90 % reduction against *S. aureus* and a relevant 98 % of antiviral activity was verified.

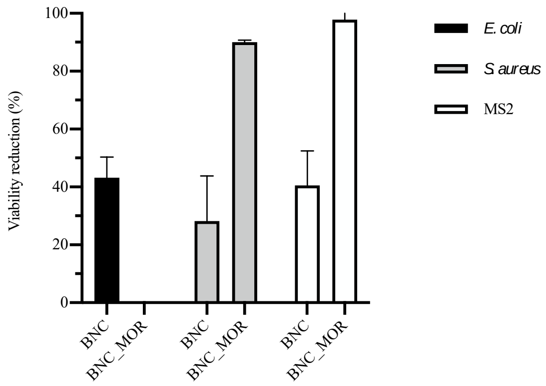

Figure 2. Antimicrobial action of BNC (control) and MOR modified BNC (BNC_MOR).

Flame retardancy properties

BNC was used as control during the flammability tests. BNC took 3.6 seconds to completely burn. Therefore, according to the Test Criteria Specimen Classification, BNC is a Class 2 textile. BNC_MOR sample did not burn, clearly denoting the effectiveness of MOR as flame retardant. Zeolites are often used in synergy with additional flame retardant additives [9,10]. To the authors knowledge this is the first work describing the sole use of a zeolite as a highly effective fire retardant. This result may be due to the incorporation of MOR within the nanofibrous structure of BNC. Thus, no adjuvants are required in combination with MOR, as needed in macrostructure textiles.

CONCLUSION

The BNC functionalization through incorporation of MOR zeolite has displayed an excellent improvement of flame retardancy properties. Furthermore, BNC_MOR exhibited nearly 99 % of antiviral activity against an encapsulated virus. Therefore, a multifunctional nanomaterial was obtained in a single step using a sustainable approach. No aggressive chemicals were use nor problematic effluents were produced, since BNC is generated by bacteria and MOR waste may be recovered through evaporation. Thus, BNC_MOR may be used in: Hospital, automotive and military textiles applications.

ACKNOWLEDGMENT

The authors acknowledge the Portuguese Foundation for Science and Technology (FCT), FEDER funds by means of Portugal 2020 Competitive Factors Operational Program (POCI) and the project UID/CTM/00264/2021 of Centre for Textile Science and Technology (2C2T), funded by national funds through FCT/MCTES. In addition, the authors Liliana Melro and Rui D. V. Fernandes acknowledge FCT, Portuguese Ministry of Science Technology and Higher Education, European Social Fund and European Union PhD grants 2020.04919.BD and SFRH/BD/145269/2019. PTDC/CTM, TEX/28295/2017, and PTDC/CTM-TEX/1213/2020, funded by FCT, FEDER, COMPETE, and MCTES.

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