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## 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  $\text{Na}_8\text{Al}_8\text{Si}_{40}\text{O}_{96}\cdot n\text{H}_2\text{O}$ . 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, hydroisomerization, 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 (dH<sub>2</sub>O) 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<sub>2</sub>O 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].

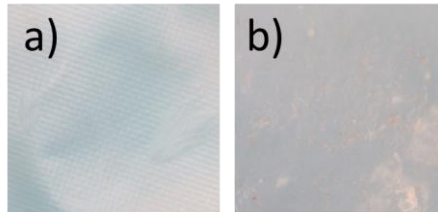
*Contact inactivation* - Bacteria inoculums were prepared in TSB and incubated overnight at 37 °C and 120 rpm. Each test was carried out using an initial concentration of  $1.0 \times 10^7$  CFUs/mL for the bacteria and  $1.0 \times 10^7$  PFUs/mL for the virus. BNC\_MOR membranes were evaluated quantitatively 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<sup>-1</sup>, over a range 400–4000 cm<sup>-1</sup>. 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

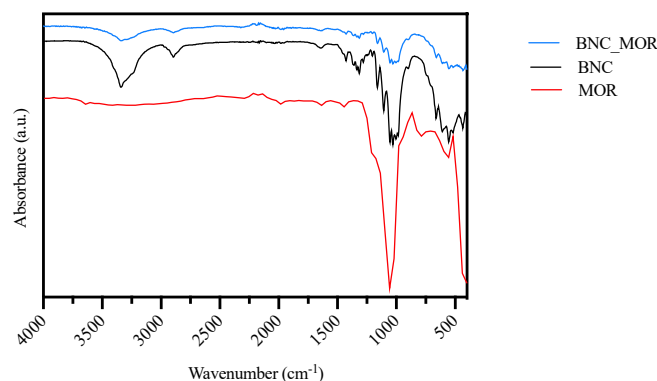
Following exhaustion, the BNC and BNC\_MOR samples were left to dry at room temperature. As observed Figure 1, when mordenite is incorporated in BNC no considerable differences are observed, the BNC\_MOR just became slightly darker. Thus, the aesthetical properties were not drastically affected.



**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*

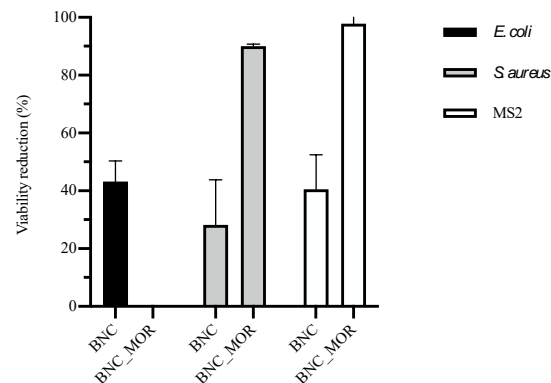
BNC\_MOR samples exhibit characteristic absorbance bands of pristine BNC, hydroxyl stretching vibration ( $3353\text{ cm}^{-1}$ ) and aldehyde stretching ( $2916\text{ cm}^{-1}$ ) [5]. Mordenite zeolite presents a strong T–O stretching vibration band ( $\sim 1057\text{--}1070\text{ cm}^{-1}$ ), where T is commonly silicon and aluminum. Other bands appear near  $787\text{ cm}^{-1}$  (amorphous  $\text{SiO}_2$ ),  $555\text{ cm}^{-1}$  (feldspar) and  $400\text{ cm}^{-1}$  (Si–O–Si bending vibration) [7]. BNC\_MOR presents typical pristine BNC ( $3353\text{ cm}^{-1}$  and  $2916\text{ cm}^{-1}$ ). 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 ( $4000\text{--}400\text{ cm}^{-1}$ ).**

### *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 used 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.

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## REFERENCES

- [1] Bourbigot S., *Flame retardancy of textiles: new approaches*, Advances in Fire Retardant Materials 2008, pp. 9-40.
- [2] Hincapie B.O., Garces L.J., Zhang Q., Sacco A., Suib S.L., *Synthesis of mordenite nanocrystals*, Microporous and Mesoporous Materials 2004, vol. 67, no 1, pp.19-26.
- [3] Klemm D., Kramer F., Moritz S., Lindström T., Ankerfors M., Gray D., Dorris A., *Nanocelluloses: A New Family of Nature-Based Materials*, Angewandte Chemie International Edition 2011, vol. 50, no 24, pp. 5438-5466.

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- [4] Padrão J., Zille A., *Surface Chemistry of Nanocellulose and Its Composites* [in:] Kumar D. (Ed.), *Nanocellulose and its composites for water treatment applications*, CRC Press, 2021, p. 230.
- [5] Padrão J., Ribeiro S., Lanceros-Méndez S., Rodrigues L.R., Dourado F., *Effect of bacterial nanocellulose binding on the bactericidal activity of bovine lactoferrin*, *Heliyon* 2020, vol. 6, no 7.
- [6] Padrão J., Nicolau T., Felgueiras H.P., Calçada C., Veiga M.I., Osório N.S., Martins M.S., Dourado N., Taveira-Gomes A., Ferreira F., 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, no 8.
- [7] Sakizci M., Özgül Tanriverdi L., *Influence of acid and heavy metal cation exchange treatments on methane adsorption properties of mordenite*, *Turkish Journal of Chemistry* 2015, vol. 39, pp. 970- 983.
- [8] Torres-Giner S., Torres A., Ferrándiz M., Fombuena V., Balart R., *Antimicrobial activity of metal cation-exchanged zeolites and their evaluation on injection-molded pieces of bio-based high-density polyethylene*, *Journal of Food Safety* 2017, vol. 37, no 4.
- [9] Reis Bernardes F., Jakeline Cunha Rezende M., de Oliveira Rodrigues V., Sandra Veiga Nascimento R., Pereira da Silva Ribeiro S., *Synthesis and Application of H-ZSM-5 Zeolites with Different Levels of Acidity as Synergistic Agents in Flame Retardant Polymeric Materials*, *Polymers* 2019, vol. 11, no 12.
- [10] Wang M.Z., Bi Y., Sun W.J., Ji H.P., Li L., *Synergistic Effect of Zeolite on Bonding Strength of Flame Retardant Plywood*, *Applied Mechanics and Materials* 2012, pp.193-194.