Cellulose Acetate Modification Towards Antibiofilm Properties via Chemical Attachment of Quaternary Ammonium Compounds using Supercritical CO_2

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1. Introduction

There is an urgency to develop novel materials capable of preventing the adherence of microorganisms to their surface. Such materials with antibiofilm properties are needed in hospitals and public places, animal farms and veterinary hospitals, and biofouling prevention. Biofouling is the phenomenon of adhesion and the growth of microorganisms on surfaces in contact with water. It poses a significant problem for filtration processes, water treatment units, bioreactors, and ships performance (marine biofouling). High-pressure techniques such as supercritical solvent impregnation and grafting in the supercritical phase allow for the modification of a solid matrix throughout the whole volume and production of materials of unique properties in an environmentally friendly way. Grafting involves the chemical attachment of an active compound to a solid matrix, ensuring its long-lasting properties. Grafting in supercritical carbon dioxide ($scCO_2$) has been reported as an efficient tool in the production of materials with antibacterial[1], and recently also antibiofilm properties[2] . This study aims to investigate the potential of cellulose acetate (CA) grafting with quaternary ammonium compounds (QAC) for acquiring antibiofilm properties. Two QAC were synthesized, and the grafting conditions were investigated. The grafting was performed via hexamethylene diisocyanate (HDI) as a linker[1]. Obtained materials were analyzed using FTIR, SEM and Ion microscopy, DSC analyses, contact angle measurements, and standardized microbiological procedures to evaluate antibiofilm properties.

2. Materials and Methods

N-(2-Hydroxyethyl)-N,N-dimethylundecan-1-aminium Bromide (QAC 1) was synthesized from 2-dimethylaminoethanol and 1-bromoundecane. N-(11-Hydroxyundecanyl-N,N-dimethyltetradecan- 1-aminium Bromide (QAC 2) was synthesized from N,N-dimethyltetradecylamine and 11-bromo-1-undecanol[1]. The chemical structure of the obtained compounds was confirmed 1H NMR and Thin-layer chromatography (TLC). A high-pressure view cell was used to attach the linker to hydroxyl groups of CA in the first step and the QAC to the functionalized CA in the next. The reaction time and conditions (pressure and temperature) were investigated for both steps. The attachment of the linker and QACs to CA was confirmed FTIR. The modification impact on the polymer was investigated by SEM, SEM-FIB (to obtain cross-sections), and DSC analyses. The contact angle measurements aimed to investigate hydrophobicity change. Standardized microbiological tests (biofilm quantification) were performed with *Listeria monocytogenes, Bacillus cereus, Escherichia coli, Salmonella enteritidis, Staphylococcus aureus,* and methicillin-resistant *Staphylococcus aureus* MRSA.

3. Results and discussion

NMR and TLC studies have proven the synthesis of desired quaternary ammonium compounds. The reaction conditions of 70°C and 30 MPa with a duration of 6 h and the decompression rate of 0.33 MPa/min were appropriate for both steps. A grafting degree of around 5% was obtained. SEM analyses revealed a considerable change in the appearance of the polymer surface (Fig. 1). However, ion beam microscopy (SEM-FIB) showed that the material's inner structure remained compact. FTIR analyses of the cross-section confirmed that the modification occurred throughout the whole volume of the polymer. DSC analysis

showed decreased glass transition temperature and increased melting temperature due to the conversion. The melting enthalpy decreased slightly after attachment of the linker and was significantly reduced after grafting QACs. Similarly, the degree of crystallinity decreased from 15.5% and 15.0% after the first grafting step and further decreased to 4.1% and 2.8% after grafting with QAC 1 and QAC 2, respectively. These results can be explained by the loss of the hydrogen bonding between polymer chains that existed in the neat CA due to the modification. The same led to the change in the appearance of the polymer's surface (Fig. 1). The contact angle measurements revealed a more hydrophobic nature of grafted material. Recorded contact angle values for pure CA, CA with the linker, CA grafted with QAC 1, and CA grafted with QAC 2 were 73°, 100°, 110°, and 112°, respectively. The microbiological analyses revealed strong antibiofilm properties of the materials obtained. It was shown that QAC 2 provided more intense activity with no bacteria attached to the surface after 24 h for all investigated strains. The polymer grafted with QAC 1 showed a slight attachment of *L. monocytogenes* and MRSA with an adhesion reduction (compared to control) of 94.4% and 96.4%, respectively.

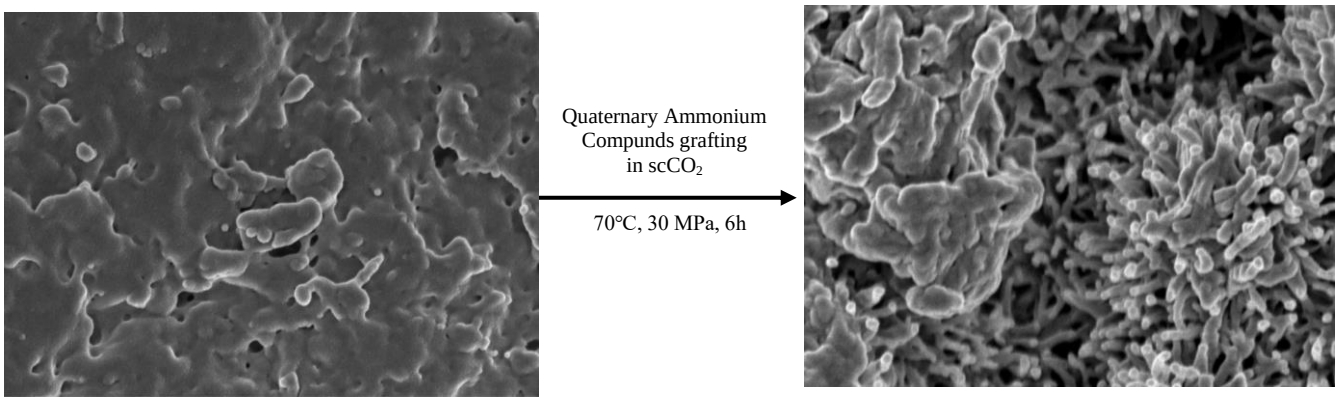

Fig. 1. CA surface before and after the modification

4. Conclusions

The study showed the feasibility of the proposed method to produce cellulose acetate-based material with strong antibiofilm properties against six tested strains. The process parameters were defined on the laboratory scale. The analyses showed that the modification occurred throughout the polymer volume, decreasing its crystallinity. The material grafted with QAC 2 showed zero bacterial adhesion for all strains, including MRSA, and has excellent potential for further studies on its application in hospitals and biofouling control.

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References

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