Characterization of active chitosan/hydroxypropyl methylcellulose/orange cellulose nanocrystals films enriched with LAE for food packaging applications

UNIMORE UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

Francesco Bigi *, Enrico Maurizzi, Heinz Wilhelm Siesler, Andrea Pulvirenti, Hossein Haghighi

*Corresponding author: francesco.bigi@unimore.it
Department of Life Sciences, via Amendola 2, 42122 Reggio Emilia, Italy

foods MDPI

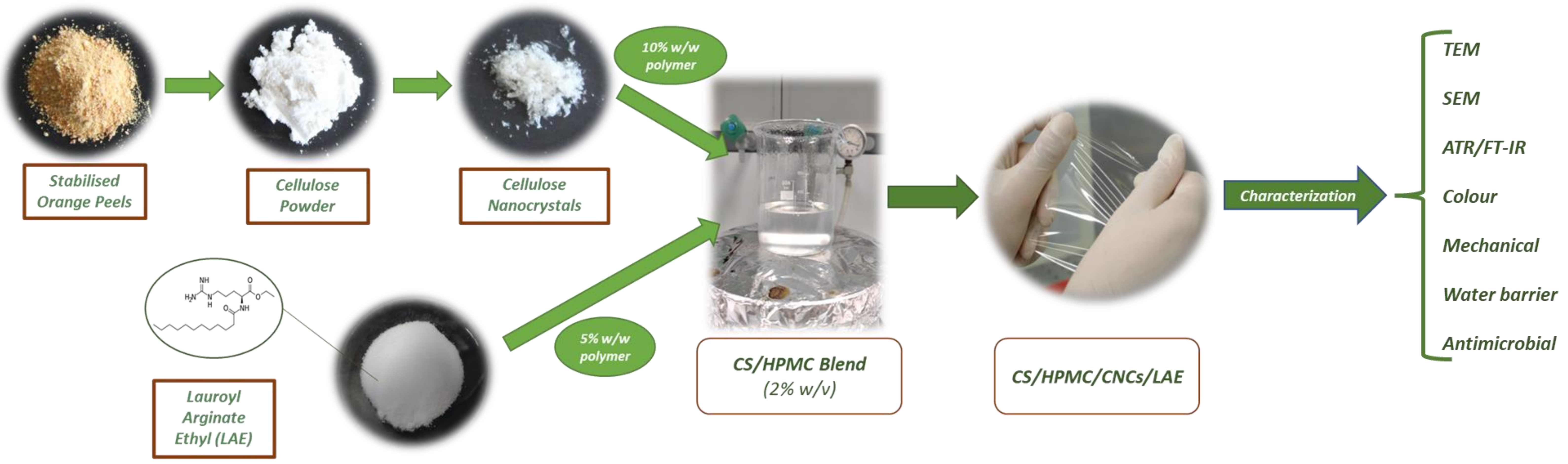
State of the Art

The social awareness about the ecological impact of petroleum-based plastics is rapidly growing. Consumers are also demanding fresh and healthy food products free of synthetic additives and preservatives [1]. In this context, active biodegradable films based on chitosan/hydroxypropyl methylcellulose blend (CS/HPMC) have emerged as a valuable alternative to synthetic packaging [2].

Enrichment of packaging materials with active compounds represents a novel concept to enhance food safety and shelf-life. Recently, lauroyl arginate ethyl (LAE) is considered as one of the most effective antimicrobial compounds with a wide range of activity against food pathogens and spoilage microorganisms [3]. In addition, the polymer matrix can be reinforced with nanomaterials such as cellulose nanocrystals (CNCs) to enhance the technological and functional performances of the packaging system. For this purpose, agricultural by-products represent promising cellulosic feedstocks to extract CNCs due to their renewability and low price [4].

This study aimed to produce CNCs from orange peels as a common industrial by-product. Then, extracted CNCs were applied as reinforcing agents to CS/HPMC films enriched with LAE. The effect of CNCs (10% w/w of biopolymer) and LAE (5% w/w of biopolymer) on the structural, functional, and antimicrobial properties of the obtained films was evaluated for their potential application in food packaging sector.

Materials and Methods



Results and Discussion

TEM and SEM Analysis

CNCs displayed needle shapes morphology (Fig. 1a), with average length and width of 500 nm and 40 nm corresponding to an aspect ratio of 12.5. Scanning electron microscopy illustrated the structural integrity of CS/HPMC blend films and compatibility between CS/HPMC with CNCs and/or LAE. Active films containing LAE revealed small discontinuities mainly due to the partial release of this compound on the film surface. A rough surface with small aggregates was observed for films containing CNCs (Fig. 1b) due to the agglomeration of the nanocrystals.

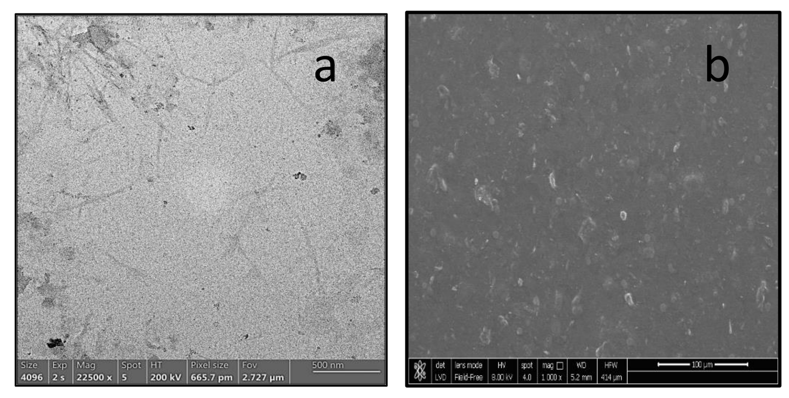


Figure 1: (a) TEM image of cellulose nanocrystals; (b) SEM image of CH/HPMC/orange CNCs film with LAE.

ATR/FT-IR

The successful incorporation of CNCs and/or LAE was confirmed by Fourier-transform infrared spectroscopy (Fig. 2). The new absorption bands appeared at 2854 cm^{-1} and 1739 cm^{-1} after LAE incorporation, corresponding to the contributions of anti-symmetric (CH_2) / symmetric (CH_2) and C=O stretching vibrations (Fig. 2b). Besides, a shift of the peak at 3346 cm^{-1} to 3335 cm^{-1} was observed after addition of CNCs (Fig. 2c) suggesting that hydrogen bonding took place between hydroxyl groups of the CNCs and CS/HPMC matrix.

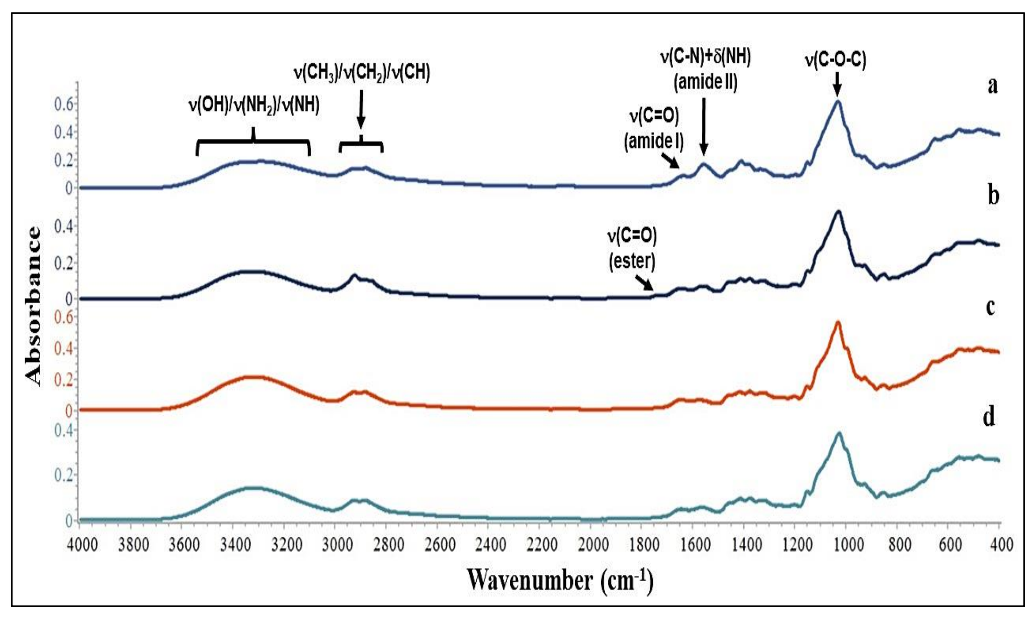


Figure 2: ATR/FT-IR spectra of films based on: a) CS/HPMC, b) CS/HPMC/LAE, c) CS/HPMC/CNCs, and d) CS/HPMC/CNCs/LAE.

Antimicrobial Activity

Presence of LAE in CS/HPMC film inhibited the growth of four major foodborne bacterial pathogens including *E. coli*, *S. enterica*, *L. monocytogenes*, and *P. fluorescens* (Tab. 1). LAE acts as cationic surfactant on the cytoplasmic membrane of Gram-positive and Gram-negative bacteria affecting the membrane potential and the cytoplasm permeability.

Functional Properties

Addition of CNCs significantly increased the tensile strength (TS) and elastic modulus (EM) of the films CS/HPMC film (Tab. 1). This effect may be ascribed to the inter- and intra-molecular interactions between the hydroxyl functionalities on the CNCs surface and the CS/HPMC blend to form hydrogen bonds filling the free spaces within the polymer chains. Addition of LAE notably increased the film elasticity (E) and reduced rigidity. This effect was related to the plasticizing effect of LAE acting as an emulsifier and reducing the adhesion forces of the film matrix. The water vapor permeability (WVP) of the CS/HPMC film was significantly reduced by the addition of CNCs due to the creation of a tortuous three-dimensional frame slowing down the diffusion of water molecules while this value was increased by addition of LAE. ΔE* of the films varied from 7.5 to 10.8. The addition of CNCs and LAE to film matrix increased the ΔE* ($p<0.05$). This increase could be related to the colorimetric parameter b* and the variation in film thickness induced by the CNCs and/or LAE (data are not shown).

Table 1: Tensile strength (TS), elongation at break (E), elastic modulus (EM), water vapour permeability (WVP), ΔE, and inhibition zone diameters of films based of films based on: a) CS/HPMC, b) CS/HPMC/LAE, c) CS/HPMC/CNCs, and d) CS/HPMC/CNCs/LAE.

Film properties	CS/HPMC	CS/HPMC/CNCs	CS/HPMC/LAE	CS/HPMC/CNCs/LAE
TS (MPa)	17.5 ± 1.0^{a}	25.4 ± 2.7^{b}	15.1 ± 0.9^{a}	26.4 ± 1.4^{b}
E (%)	18.9 ± 0.9^{a}	19.9 ± 1.6^{a}	23.9 ± 1.0^{b}	27.8 ± 1.9^{c}
EM (%)	644.7 ± 25.2^{c}	705.8 ± 57.2^{d}	407.0 ± 28.9^{a}	529.1 ± 48.8^{b}
WVP (g mm/kPa day m^2)	7.2 ± 0.5^{b}	5.8 ± 0.3^{a}	9.5 ± 0.7^{c}	6.8 ± 0.5^{ab}
ΔE	7.5 ± 0.6^{a}	10.8 ± 0.4^{b}	7.8 ± 0.7^{a}	10.0 ± 1.0^{b}
***S. enterica* (mm)**	N.D.	N.D.	0.9 ± 0.09^{b}	0.5 ± 0.07^{a}
***E. coli* (mm)**	N.D.	N.D.	4.4 ± 0.4^{b}	3.4 ± 0.4^{a}
***L. monocytogenes* (mm)**	N.D.	N.D.	6.7 ± 0.6^{a}	6.5 ± 0.6^{a}
***P. fluorescens* (mm)**	N.D.	N.D.	8.5 ± 0.7^{b}	5.7 ± 0.4^{a}

Values are given as mean ± SD (n = 3). N.D. means not detected. Different lowercase letters in the same raw indicate significant differences (p<0.05).

Conclusions

The obtained results suggest the possibility to employ film based on CS/HPMC/CNCs/LAE as a green and environmentally friendly approach for partial substitution of the conventional plastics for packaging foods which are sensitive to microbiological decay and spread of food-borne pathogens.

References

1. Costa, S.M., Ferreira, D.P., Teixera, P., Ballesteros, L.F., Teixera, J.A., & Fanguiero, R. (2021). Active natural-based films for food packaging applications: The combined effect of chitosan and nanocellulose. International Journal of Biological Macromolecules, 177, 241-251. https://doi.org/10.1016/j.ijbiomac.2021.02.105
2. Bigi, F., Haghighi, H., Siesler, H. W., Licciardello, F., & Pulvirenti, A. (2021). Characterization of chitosan-hydroxypropyl methylcellulose blend films enriched with nettle or sage leaf extract for active food packaging applications. Food Hydrocolloids, 120, 106979. https://doi.org/10.1016/j.foodhyd.2021.106979
3. Rubilar, J. F., Candia, D., Cobos, A., Díaz, O., & Pedreschi, F. (2016). Effect of nanoclay and ethyl-Nα-dodecanoyl-L-arginate hydrochloride (LAE) on physicomechanical properties of chitosan films. Lebensmittel-Wissenschaft und -Technologie- Food Science and Technology, 72, 206–214. https://doi.org/10.1016/j.lwt.2016.04.057.
4. Coelho, C. C. S., Silva, R. B. S., Carvalho, C. W. P., Rossi, A. L., Teixeira, J. A., Freitas-Silva, O., & Cabral, L. M. C. (2020). Cellulose nanocrystals from grape pomace and their use for the development of starch-based nanocomposite films. International Journal of Biological Macromolecules, 159, 1048–1061. https://doi.org/10.1016/j.ijbiomac.2020.05.046