proceedings

MDPI

Abstract

Glycodinameric Hydrogels Based on Chitosan and a Vanillin Isomer †

Manuela Maria Iftime [1], Florentina Georgescu [2], Alina Nicolescu [1], Luminita Marin [1,*] and Florin Oancea [3,*]

[1] "Petru Poni" Institute for Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, 700487 Iasi, Romania; ciobanum@icmpp.ro (M.M.I.); alina@icmpp.ro (A.N.)
[2] Research & Development Department, Enpro Soctech Com srl, Str. Elefterie 51, 050524 Bucharest, Romania; florentina.georgescu@enpro.ro
[3] Bioresource Departement, National Institute for Research & Development in Chemistry and Petrochemistry-ICECHIM, Spl. Independentei 202, 060201 Bucharest, Romania
* Correspondence: lmarin@icmpp.ro (L.M.); florin.oancea@icechim.ro (F.O.)
† Presented at the 19th International Symposium "Priorities of Chemistry for a Sustainable Development", Bucharest, Romania, 11–13 October 2023.

Keywords: hydrogels; chitosan; vanillin; antifungal activity; self healing

Hydrogels are a promising class of materials addressing a plethora of applications in biomedicine, environmental protection and agriculture [1–3]. Chitosan-based hydrogels are particularly important due to their sustainable nature and biodegradability, accounting for a circular bioeconomy. In addition, chitosan is biocompatible, non-toxic and has antimicrobial activity, properties which make it a work-bench to develop new biomaterials which satisfy the requirements of contemporary society. In this view, the goal of this study was the development of new chitosan hydrogels with antifungal activity which can be further used as a matrix to build soil conditioners to deliver plant biostimulants in a prolonged manner. Low-molecular-weight chitosan and 5-methoxysalicylaldehyde were analyzed using 1H-NMR, FTIR and UV-vis spectroscopy, SEM and POM microscopy, thermogravimetrical analysis, X-ray diffraction, swelling and biodegradation investigation, cytotoxicity and microbiological tests. The new hydrogels were synthesized by crosslinking chitosan with a vanillin isomer, 5-methoxysalicylaldehyde using an imination reaction followed by the self-assembling of the newly formed imine units. The crosslinking pathway was confirmed by FTIR and 1H-NMR spectroscopy, which proved the formation of imine bonds, and X-ray diffraction and POM microscopy, which proved supramolecular self-ordering. When analyzed using an MTT assay on normal dermal fibroblasts, the hydrogels showed a lack of toxicity for a molar ratio of the functional groups (amine/aldehyde) of 1.5, 2 and 3. The swelling ratio of the hydrogels depended on the pH of the media, and it was lower in media with basic pH, up to 20 g/g, and higher in media with neutral and acidic pH, up to 150 g/g. They proved biodegradability in the presence of lysozyme, reaching a mass loss of 35% in 18 days. Under mechanical stress, the hydrogels were broken and completely rebuilt when the stress was removed, indicating self-healing ability (Figure 1a). SEM microscopy revealed a porous morphology formed from interconnected pores with diameters around 85–100 µm—Figure 1b. TGA indicated the increase of the thermal stability assessed to the strong intermolecular forces. The hydrogels are biodegradable (Figure 1c) and cytocompatible (Figure 1d). When in contact with different microbial strains, the hydrogels showed strong antifungal activity against *C. albicans*, *P. chrysogenum*, *C. glabrata* and *C. cladosporioides*, as determined by disk diffusion assay Figure 1 e is a representative image for inhibition zone the case of *C. albicans*.

check for updates

Citation: Iftime, M.M.; Georgescu, F.; Nicolescu, A.; Marin, L.; Oancea, F. Glycodinameric Hydrogels Based on Chitosan and a Vanillin Isomer. *Proceedings* **2023**, *90*, 42. https://doi.org/10.3390/proceedings2023090042

Published: 25 December 2023

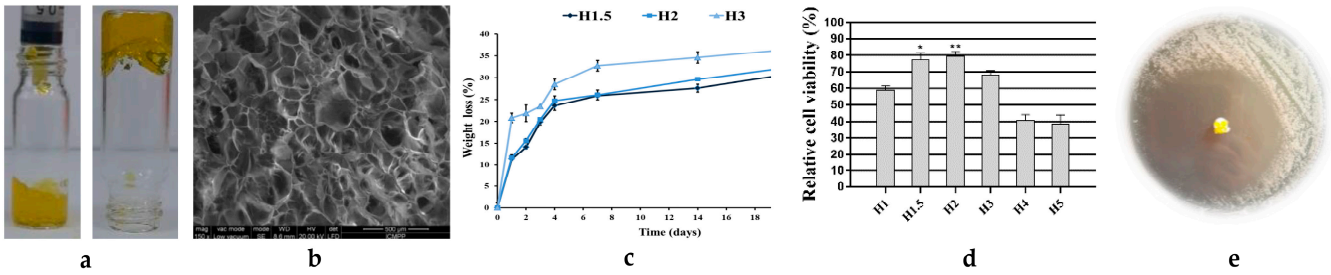

Figure 1. Representative images of the hydrogels and their properties. (**a**) Visual assessment of the self-healing ability of the hydrogels; (**b**) Scanning electron microscopy image (SEM) of porous xerogel; (**c**) In vitro biodegradation profiles of representative hydrogels; (**d**) Cell viability of normal human dermal fibroblasts (NHDF) after 24 hours exposure to hydrogels. Bars represent the standard error. * $p < 0.05$ and ** $p < 0.01$; (**e**) Representative image for inhibition zone the case of *C. albicans*.

New naturally originating hydrogels with good biocompatibility and antifungal properties were prepared by a simple and easy method from chitosan and a vanillin isomer. It was demonstrated that the driving force of hydrogelation relies on the forming of covalent reversible imine bonds and supramolecular organization of the newly formed imine units in clusters playing the role of crosslinking nodes. An optimal amount of aldehyde used for chitosan crosslinking generated hydrogels with suitable biocompatibility and remarkable antifungal activity. These hydrogels presented porous morphology and consequently good swelling in various media, indicating good oxygen permeation and liquid drainage. In addition, they were biodegradable and presented self-healing behavior, indicating easy manipulation in view of further applications.

Author Contributions: Conceptualization, L.M.; methodology, M.M.I., F.G., A.N. and L.M.; validation, L.M., A.N. and F.G.; investigation, M.M.I., A.N. and L.M.; resources, F.O.; data curation, A.N.; writing—original draft preparation, M.M.I.; writing—review and editing, L.M. and F.O.; visualization, L.M.; supervision, L.M.; project administration, F.O.; funding acquisition, F.O. All authors have read and agreed to the published version of the manuscript.

Funding: The research leading to these results has received funding from the NO Grants 2014-2021, under Project RO-NO-2019-0540 (STIM4+), contract 14/2020.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author, L.M.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Iftime, M.M.; Morariu, S.; Marin, L. Salicyl-imine-chitosan hydrogels: Supramolecular architecturing as a crosslinking method toward multifunctional hydrogels. *Carbohydr. Polym.* **2017**, *165*, 39–50. [CrossRef] [PubMed]
2. Iftime, M.M.; Rosca, I.; Sandu, A.I.; Marin, L. Chitosan crosslinking with a vanillin isomer toward self-healing hydrogels with antifungal activity. *Int. J. Biol. Macromol.* **2022**, *205*, 574–586. [CrossRef] [PubMed]
3. Cibotaru, S.; Ailincai, D.; Adreica, B.I.; Cheng, X.; Marin, L. TEGylated Phenothiazine-Imine-Chitosan Materials as a Promising Framework for Mercury Recovery. *Gels* **2022**, *8*, 692. [CrossRef]