chemistry proceedings

MDPI

Abstract

Synthesis of Silver Nanoparticles Embedded in Micro-Hydrogel Particles by Electron Beam Irradiation †

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† Presented at the 17th International Symposium "Priorities of Chemistry for a Sustainable Development" PRIOCHEM, Bucharest, Romania, 27–29 October 2021.

Abstract: This study focuses on synthesizing a hybrid micro-hydrogel with antibacterial properties by electron beam irradiation. The micro-hydrogel matrix is based on biocompatible polymer poly(vinyl)alcohol functionalized with antibacterial compounds: graphene oxide and silver nanoparticles The polymer composites were synthesized by irradiation with an electron beam at 10, 25, 50 kGy absorbed dose to form silver nanoparticles.

Keywords: hybrid micro-hydrogel; poly(vinyl)alcohol; graphene oxide; silver nanoparticles; electron beam irradiation; antibacterial properties

Citation: Ion, I.; Stancu, E.; Mitu, C.M.; Marinescu, V.; Lungulescu, E.M.; Nicula, N.O. Synthesis of Silver Nanoparticles Embedded in Micro-Hydrogel Particles by Electron Beam Irradiation. *Chem. Proc.* **2022**, *7*, 22. https://doi.org/10.3390/chemproc2022007022

Academic Editors: Mihaela Doni, Florin Oancea, Zina Vuluga and Radu Claudiu Fierăscu

Published: 3 March 2022

1. Introduction

This work aims to produce a multifunctional hybrid micro-hydrogel (HMH) that can mimic the biology of human tissues in terms of structure, function, and performance. For this reason, a poly(vinyl)alcohol (PVA) matrix was chosen and functionalized with pyrrole (Py) to improve conductivity, with graphene oxide GO and silver nanoparticles (AgNPs) as antibacterial compounds [1–3]. Polypyrrole (PPy) is often used in biomedical applications (e.g., biosensors, hydrogels, and drug delivery) because of its good biocompatibilities and environmental and thermal stability [4–6]. PPy is an electrically conductive polymer with electrical conductivity ranging between 10 and 100 s/cm [4]. PPy has the disadvantages of being brittle and mechanically unstable [5].

2. Materials and Methods

PVA hydrogel was synthesized by an electron beam irradiation (EBR) of 20 mL PVA solution with a concentration of 10% (wt./vol.) and molecular mass Mw = 400,000 g/mol, GO and silver salt with a concentration of 1 mg/mL, functionalized with Py and iron salt. HMH codification is presented in Table 1. GO was synthesized via the Hummer modified method [7,8]. The irradiation experiments were performed at National Institute for Laser, Plasma and Radiation Physics using its ALID-7- Linear Electron Accelerator of traveling-wave type, operating at a wavelength of 10 cm. The accelerating structure is a disk-loaded tube operating in the $\pi/2$ mode [9]. In our experiments, the electron beam dose rate was fixed at 2.5 kGy/min to accumulate doses between 10 kGy and 50 kGy.

The morphological and structural characteristics of HMH were investigated through UV-Vis Spectroscopy, Differential Scanning Calorimetry (DSC), and Scanning Electron

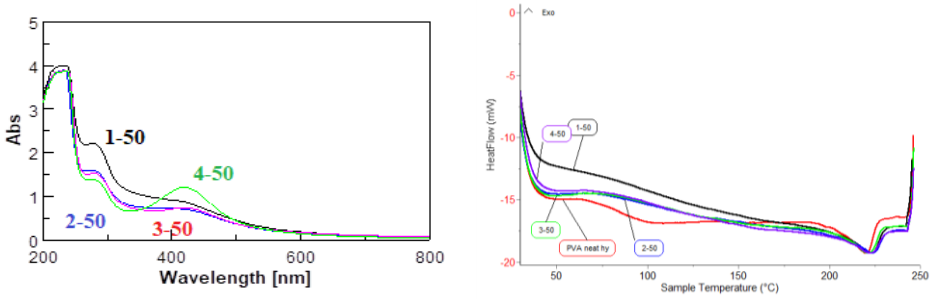
Microscopy (SEM). The UV-Vis spectrometry measurement was performed on UV-Vis-NIR spectrophotometer of V570 type (Jasco). The DSC analysis was performed with a SETARAM 131 EVO DSC-instrument. Imagistic investigations were performed on Auriga Carl Zeiss Workstation-SEM.

By definition, a hydrogel must contain at least 10% water [10]. The solid residue obtained after drying at 80 °C to the constant mass of the hydrogel led to mass losses between 83.86–90.96%, with an average of 85.96%.

Table 1. UV-Vis spectra parameters of HMH versus irradiation dose.

HMH Codification	Batch 10 kGy		Batch 25 kGy		Batch 50 kGy	
	λmax [nm]	Abs [a.u.]	λmax [nm]	Abs [a.u.]	λmax [nm]	Abs [a.u.]
1.HMH PVA-Py-Fe-Ag	-	-	-	-	380	0.73
2.HMH PVA Py-Fe-Ag-GO	-	-	-	-	397.5	0.68
3.HMH PVA Py-Ag	417	1.24	418.5	0.84	419	0.7
4.HMHPVA Py-Ag-GO	416	1.59	417.5	1.50	419.5	1.21

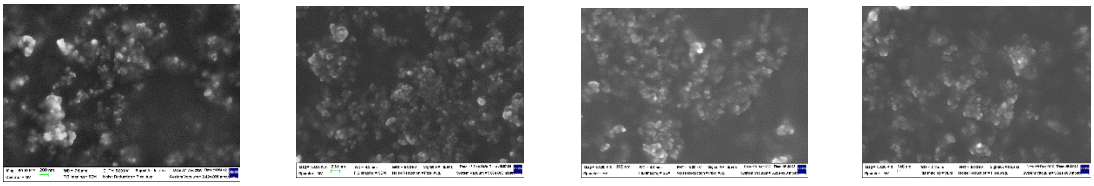
The recorded UV-Vis spectra exhibit the Surface Plasmon Resonance (SPR) peak specific for AgNps, ranging between 379.7 and 419 nm (Figure 1a). SRP for Ag Np can change its position and form depending on the size, shape, composition, solvent, and surface capping agent [11,12].



(**a**) (**b**)

Figure 1. (**a**) UV-Vis spectra of batch 50 kGy; (**b**)DSC curves for the samples irradiated at 50 kGy.

Figure 2 presents HMH cross-linked with 10 kGy absorbed. All studied HMH present AgNps covered in the polymeric materials, with the sizes of nanoparticles ranging between 20 and 100 nm. These prove the successful synthesis of AgNp by EBR.



(1). HMH PVA-Py-Fe-Ag (2). HMH PVA-Py-Fe-Ag-GO (3). HMH PVA-Py-Ag (4). HMH PVA-Py-Ag-GO

Figure 2. SEM images for hydrogel cross-linked with absorbed dose of 10 kGy.

In this paper, the DSC technique was used to investigate the glass transition temperature (T_g), melting temperature (T_m), and crystalline fraction (C.f.), as presented in Figure 1b. The T_g for the powder PVA was 119.5 °C, while that of the neat PVA hydrogel was 84.2 °C. The same significant reduction has been reported by other authors [13–15]. The irradiation process has no significant T_g modification for the 10 kGy dose, with T_g ranging

between 80.93 and 88.66 °C. For the 25 kGy dose, T_g ranged between 86.47 and 88.08 °C. For the 50 kGy doze, T_g ranged between 92.14 and 105.7 °C. This happened because the energy coming from the irradiation process determines the increase of the cross-linking phenomenon, especially an increase in cross-linking density. An increase in the crosslinking density impedes the movement of the polymer chain, and T_g increases. In conclusion, the cross-linking density is, in general, correlated with dose [16–18].

T_m for the PVA powder was 221.9 °C, while that of neat PVA hydrogel was 220.4 °C. The differences in T_m values are very small, ranging between 221.29 and 227.29 °C for all irradiation doses/all composition types studied, with average values per absorbed dose as follows: 226.29 °C for 10 kGy, 225.55 °C for 25 kGy, and 222.87 °C for 50 kGy. The T_m values are in good agreement with other reported values presented by other authors [14,15]. The addition of Py, iron salt, GO, and silver salt did not affect the thermal stability of the PVA matrix. This is because the additives are in quantities too small to affect the melting behavior of the polymer matrix, with the concentration of PVA effectively remaining constant. Previous research showed that the concentration of PVA is directly correlated with T_m [13,15].

The crystalline fraction presents an anti-correlated behavior related to irradiation dose/cross-linking density, with average values as follows: 46% for 10 kGy absorbed dose, 38% for 25 kGy absorbed dose, and 32% for 50 kGy absorbed dose. Previous researcher showed the same trend [12].

Qualitative testing of the antimicrobial effect tested in the presence of resazurin (Figure 3) showed that the HMH have a bactericidal effect on the bacterial strains used (Escherichia coli ATCC 25922 and Staphylococcus aureus ATCC 9737), most likely due to the synergism of the bactericidal effect of GO and AgNp.

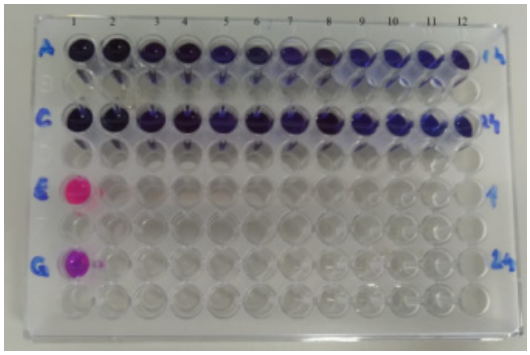


Figure 3. Qualitative testing of the antimicrobial effect of the HMH in the presence of resazurin.

3. Conclusions

AgNps was successfully synthetized by EBA, as proven by SEM images and silver SPR from UV-Vis spectra. The antimicrobial effect of AgNp/GO embedded in HMH synthesized by EBI is correlated with the dose, making it suitable as an antibacterial gel in wound dressing applications.

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

Funding: This research was supported by the projects from Position 2 of the JINR Order 322/21.05.2018, Position 3 of the JINR Order 365/11.05.2021, and Project PN 19310101-46N/2019. The irradiation experiments were supported by Project 149N/2019.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article. The data presented in this study are available in insert article.

Acknowledgments: This research was supported by the projects from Position 2 of the JINR Order 322/21.05.2018 and Position 3 of the JINR Order 365/11.05.2021. The irradiation experiments were supported by Project 149N/2019.

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

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