Structural peculiarities of PVA-AgNPs hydrogel nanocomposites irradiated by high-energy electron beam

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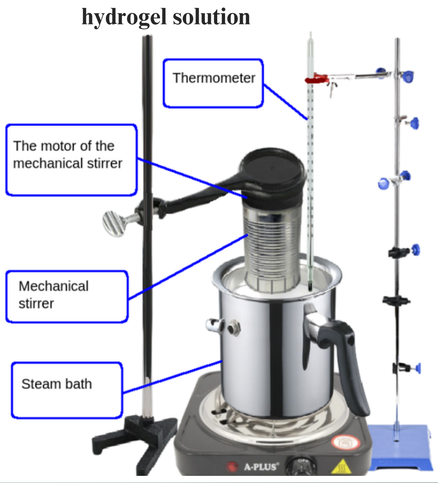
Introduction

For purpose of treatment of burns silver-containing hydrogel dressings cross-linked by high-energy electron irradiation are effectively used. Depending on the dose and the content of silver, the structure of hydrogel nanocomposite, the size and distribution of the Ag nanoparticles, reduced from silver nitrate, may change and that effects on the properties of the dressings.

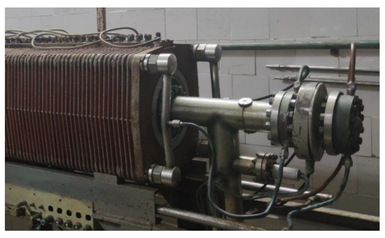
The aim of this work is to study the influence of high-energy electron beam radiation on the structure of hydrogel nanocomposites, parameters and distribution of the formed nanoparticles.

1. *Synthesis of hydrogel nanocomposites*

Installation for the preparation of a hydrogel solution



To prepare hydrogel solutions, silver nitrate (0.01%-1%) was dissolved in distilled water (85.5%-86.49%, depending on the mass fraction of $AgNO_3$), after which polyvinyl alcohol (12%) was dissolved in a steam bath at a temperature of 90°C and polyethylene glycol (1.5%) with constant stirring with a mechanical stirrer.



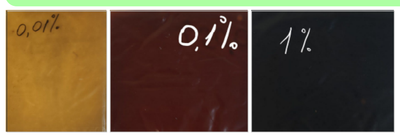
Linear electron accelerator "Electronics LEA-4", P=4 MeV

The "Electronics LEA-4" is used for the formation and provides suitable elastic characteristics of hydrogel dressings and the recovery.

2. *Characterization*

1. Light-Scattering Instrument **LiteSizer 500 (Anton Paar)** was used for particle analysis in liquid solution based on distilled water (99.89%), PVA (0.1%) and silver nitrate (0.01%) irradiated with different doses (33-198kGy)
2. **JEOL 100CX-II** was used to TEM study nanoparticles and their agglomerates in liquid solutions.
3. **XRD-7000 (Shimadzu)** was used to study the peculiarities of the structural organization of hydrogel samples by the method of automatic step-by-step scanning in the mode U=30kV, I=30mA, 2θ=3-50° at research temperatute 293±2 K.
4. **Quanta FEG 250 (ThermoFischer Scientific)** was used for SEM studies of samples dried under normal conditions in the low vacuum mode at an accelerating voltage of 5 kV.

3. *Syntheszed hydrogel nanocomposites*



The synthesized hydrogel solutions change their color depending on the composition of the samples.

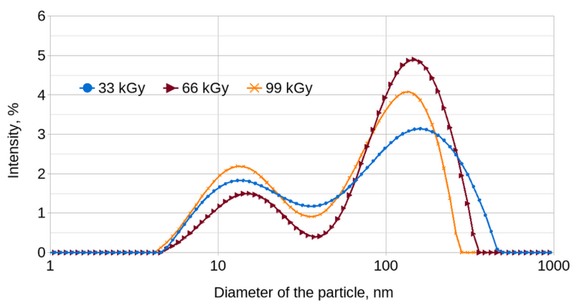
Mass fraction of silver nitrate, %	*Radiation dose, kGy*				
	33	73	99	132	165
0.01	+	+	+	+	+
0.1	+	+	+	+	+
1	+	+	+	+	+

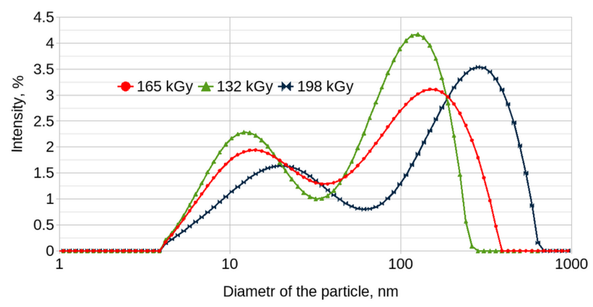
Green - the optimal doses of irradiation for the formation of hydrogel nanocomposites.

Yellow cells correspond to less elastic samples.

Red - destroyed ones (0.01% and 0.1%), viscous substances (1%).

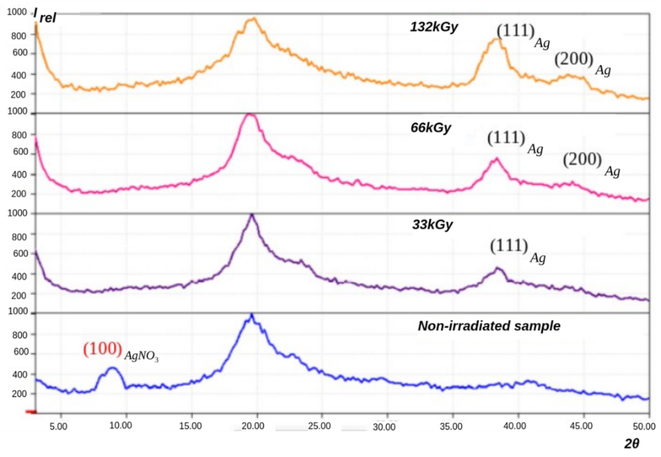
4. *Particle Analysis*





The distribution of particles by intensity is characterized by two peaks at 15 nm—20 nm and 140 nm—240 nm, depending on the radiation dose. The first peak corresponds to individual silver nanoparticles, and the second corresponds to their clusters or strongly oxidized Ag particles. The shape of the distribution of particles does not significantly depend on the dose of irradiation.

5. *XRD Analysis*



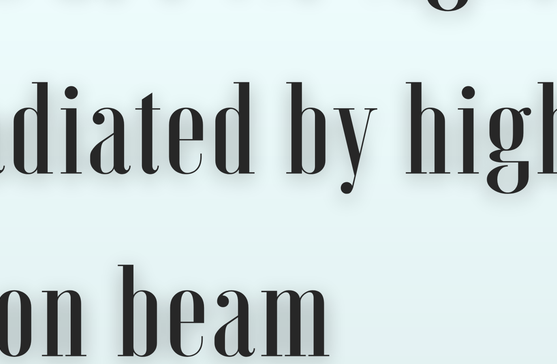
Unirradiated sample filled with silver nitrate - the peak at 2θ=9.2° - (100) for silver nitrate, forbidden for symmetry reasons. This peak may arise due to the scattering of the atomic planes of some polymer-crystal complexes, which is confirmed by the absence of such peaks in the irradiated samples [1].

33kGy - the peak at 2θ=38.2° - (111) for FCC Ag

66kGy - the peaks at 2θ=38.2° and 2θ=44.3° - (200) for FCC Ag.

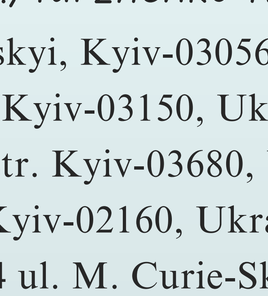
132kGy - the intensities of both peaks increased

6. *TEM Analysis*

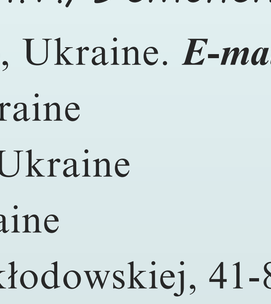


A group of particles formed in a liquid solution irradiated with a dose 33kGy.

A group of particles and an agglomerate in an oxide shell formed in a liquid solution irradiated with a dose 198kGy.

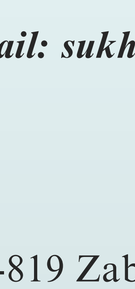


ZA ~ 110



Spherical AgNP

d≈89 nm



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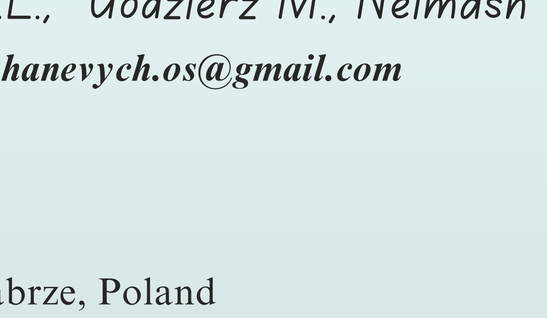
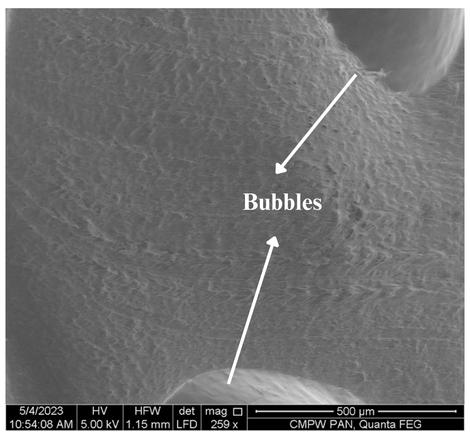


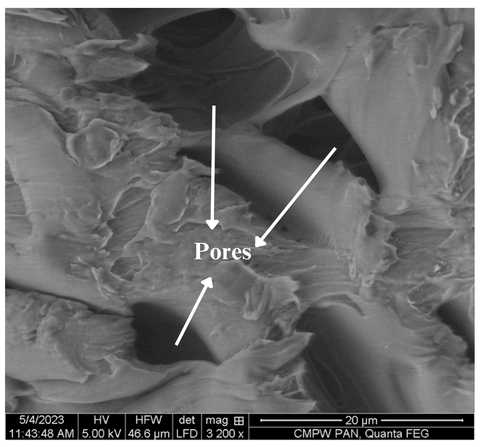
Dodecaedron Ag_2O NP. The darker area is probably a silver particle around which an oxide shall has formed

7. *SEM Analysis*

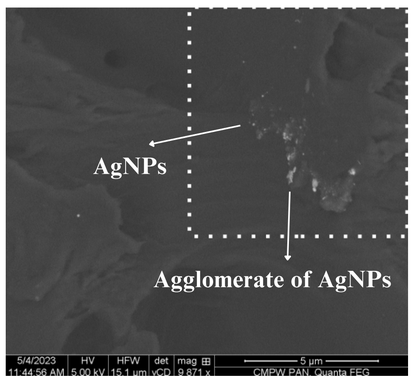


bubbles size 0.1-1 mm

Secondary electron detector



Pores size 10-30 µm



Backskattered electron detector

Mostly spherical light spots are observed.
Taking into account the results of XRD analysis, they are AgNPs.
So, silver nanoparticles with the size of 40-90 nm and their agglomerates with the size of 160-470 nm were found.

Conclusion

1. Some structural peculiarities of PVA-AgNPs nanocomposite were studied by DLS, TEM, SEM methods and XRD analysis.
2. DLS analysis confirmed the presence of nanoparticles in liquid solutions irradiated with different doses. The distribution of particles by intensity is characterized by two peaks at 15 nm—20 nm (for individual AgNPs) and 140 nm—240 nm (for agglomerates of AgNPs or strongly oxidezed AgNPs), depending on the radiation dose, but the shape of the distribution of particles doesn`t significantly depend on the dose of irradiation.
3. XRD analysis of the unirradiated sample revealed a peak characteristic of silver nitrate. When the sample is irradiated by high-energy electrons this peak disappears and the (111)FCC Ag and (200)FCC Ag peak appear. With a further dose increase, the intensities of both peaks increase confirming the reducing of Ag from silver nitrate.
4. TEM analysis revealed that in addition to Ag nanoparticles the Ag oxide presents in the irradiated samples in a form of oxide shell on the silver nanoparticles or as standalone faceted nanoparticles with the size of 30-70 nm. Probably, this oxide is formed from reduced Ag, which interacts with the products of the radiolysis of water in hydrogel irradiated by high-energy electrons.
5. SEM analysis has shown that the nanocomposite has a porous structure with the small pores size 10-30 µm able to absorb water effectively and bubbles size 0.1-1 mm, which seems appear due to cross-linking, radiolysis and reduction reactions. The pore surfaces are smooth and uniform. Silver nanoparticles with the size of 40-90 nm and their agglomerates with the size of 160-470 nm were found.

References

[1] H.M. Zidan Effect of filling and UV-irradiation on the structure and morphology of PVA films