

SYNTHESIS OF SILVER NANOPARTICLES IN HYDROGELS CROSSLINKED BY IONIZING RADIATION

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ABSTRACT

Hydrogel is defined as a polymeric material which exhibits the ability to swell and retain a significant fraction of water within its structure without dissolving the polymeric network. Silver nanoparticles (AgNPs) are used in a range of medicinal products based on hydrogels and diverse other products due to their antibacterial properties at low concentrations. The use of ionizing radiation in the production process of hydrogels of poly(*N*-vinyl-2-pyrrolidone) (PVP) and poly(vinyl alcohol) (PVA) in aqueous solutions enables the crosslinking of their polymer chains. If polymer solutions contain Ag⁺ ions, these can be reduced radiolytically to nanocrystalline silver. The objective of this study was to investigate the reduction of Ag⁺ ions by gamma-irradiation for the synthesis of AgNPs in hydrogels of PVA and PVP as main polymers and to make a comparison of the performance of the two polymeric matrices, chiefly focusing on the effect of the AgNPs' synthesis on the crosslinking of both polymers. The properties of the hydrogel matrices obtained were evaluated from tests of gel fraction, swelling in water, and stress-strain. The results of mechanical properties of PVA matrix were higher than those of PVP one whereas the latter exhibited a higher swelling degree. The reduction of silver ions was confirmed by UV-visible absorption spectrum, whose characteristics also indicated the formation of silver nanoparticles in both arrays.

Keywords: hydrogel, poly(*N*-vinyl-2-pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), silver nanoparticles

1. INTRODUCTION

Hydrogel is defined as a polymeric material which exhibits the ability to swell in the presence of water and absorb a significant fraction within its structure without dissolving the polymeric network. Additionally, it presents the advantage of low interfacial tension which may be exhibited between the surface of the hydrogel and an aqueous solution (Ratner and Hoffman, 1976).

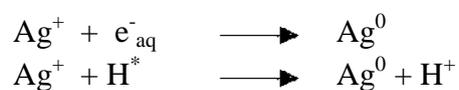
The hydrophilic gels have various industrial applications, as biomedical devices, agriculture, and many others. Hydrogels may be prepared using various polymers and different techniques. The methods of ionizing radiation are attractive for the synthesis of hydrogels because they have advantages over the use of the chemical ones, since those methods do not leave toxic residues, the process is easily controlled, they promote simultaneous sterilization, are economically competitive when compared with other more conventional methods such as chemical crosslinking, where remaining crosslinking agent, if not removed, will not allow

the use of the obtained gel in biomedical and pharmaceutical applications (Peppas et al., 2006)

Among the polymers used for synthesis of hydrogels, poly (*N*- vinyl-2-pyrrolidone) (PVP) stands out. It is a non-ionic polymer, water soluble, presents interesting biocompatible properties, and hydrogels obtained from of its aqueous solutions with the aid of radiation techniques have been used as matrices of dressings (Rosiak et al. 1986). Another polymer that can be crosslinked through radiation techniques is poly (vinyl alcohol) (PVA). It is useful in a wide variety of applications, particularly in the areas of medical and pharmaceutical science. It has a relatively simple chemical structure, is water soluble, biocompatible, and biodegradable .

Silver has a long and fascinating history for the treatment of human diseases. Colloidal silver products have been based on the dispersion and suspension of ultrafine particles of silver in nanoscale, i.e. silver nanoparticles (AgNPs). They are widely used as a valuable nanomaterial for medical staffs and hygiene fields by incorporating them in hundreds of consumer products (Lansdown, 2010).

The reactions in aqueous systems, such as hydrogels, occur between the solute and the the primary products of water radiolysis. The primary products are e^-_{aq} , OH^* , H^* , H_2 , H_2O_2 . Among these, OH radicals strongly react with the polymer, generating macroradicals that allow the crosslinking of PVP and PVA (Rosiak *et al.* 1995). On the other hand, the solvated electrons (e^-_{aq}) and the H^* atoms are strong reducing agents. Thus, they may, under certain conditions, easily reduce silver ions by leading them to the zero valence state (Sheikh et al., 2009 , Krkljes et al. , 2007a) as the following equation:



2. MATERIALS AND METHODS

2.1. Materials

Poly(*N*-vinyl-2-pyrrolidone) (PVP - Plasdone® K-90D, $\overline{M}_w =$ ca. 1,300,000 g.mol⁻¹, from ISP) ; poly(vinyl alcohol) (PVA - Vinarol STH, $\overline{M}_w =$ ca. 205,000 g.mol⁻¹, apparent viscosity ca. 40 mPa.s, aqueous solution at 4% / 20 ° C, degree of hydrolysis ca. 88%, from Clariant; reverse osmosis water and silver nitrate P.A. from Cennabras.

2.2. Hydrogels' preparation

The synthesis of the hydrogels took place from aqueous solutions of PVP (12%) and PVA (9%) using reverse osmosis water as solvent at ca. 70°C for ca. 7 h, followed by silver nitrate addition to both solutions at room temperature. After homogenization under stirring, N₂ was bubbled to remove O₂ from the solutions. The crosslinking was carried out by gamma-irradiation from a ⁶⁰Co source with a dose of 25 kGy and the dose rate of 1.8 kGyh⁻¹.

2.3. Gel fraction

The gel fraction test was performed on dry samples in quintuplicate. The extraction of the soluble fraction was effected on stainless steel bag with screen of 300 meshes dipped in distilled water, next autoclaved at 120 ° C for 2 h. After this period, the samples were dried to a constant weight, and the gel fraction was calculated by Eq.1:

$$\text{Gel fraction (\%)} = \frac{M_f}{M_0} \times 100 \quad (1)$$

where M_f is the mass of the dried sample after extraction of the soluble fraction and M_0 is the mass of dry sample before extraction.

2.4. Swelling

Swelling tests were performed on samples measuring 24 mm x 20 mm x 2 mm, in quintuplicate. The samples were immersed in 100 mL of reverse osmosis water, maintained the 30° C and weighed periodically until weight stabilization. Swelling results from each measure performed were calculated in accordance with Eq. 2:

$$\text{Degree of swelling (\%)} = \frac{M_i - M_s}{M_s} \times 100 \quad (2)$$

where M_i is the mass of the swelled hydrogel and M_s is the mass of the dry hydrogel.

2.5. UV-visible spectroscopy

Spectroscopic analyzes were performed on an equipment Varian Cary 50 at wavelength of 300-800 nm.

2.6. Stress x Strain

The mechanical properties tests were performed on a texturometer Stable Micro Systems, model TA.X Plus, using specimens measuring 100 mm x 24 mm x 2.5 mm. The tension speed was 0.833 mm.s⁻¹. A minimum of 5 specimens of each hydrogel were used.

The tension data were calculated by the equipment software from the data of the cross section area provided to each measured sample, and the results of stress and deformation were read directly on the stress-strain chart at the rupture point.

The elastic modulus was calculated according to Eq. 4 from the average of the results obtained in the straight part of each curves of stress-strain diagram, by using Hooke's law (Eq. 3):

$$\sigma = E \cdot \varepsilon \quad (3) \quad \text{and} \quad \varepsilon = \frac{\Delta L}{L_0} \quad (4)$$

where σ is the tension, ε is the strain, E is the elastic modulus, ΔL is the variation in length and $L_0 = 0.06$ m.

3. RESULTS AND DISCUSSION.

Fig. 1 are shows the average results of gel fraction and their standard deviations obtained experimentally from hydrogels synthesized with PVP and PVA.

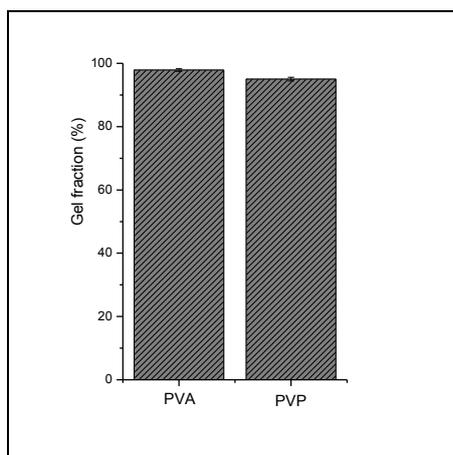


Figure 1. Gel fraction of hydrogels of PVA and PVP with colloidal silver.

The results indicate a high degree of crosslinking for both hydrogels synthesized. The gel fraction obtained from PVA and PVP hydrogels are very close indicating that, despite the difference in the concentration of polymer, the gel fraction difference was not significant.

Despite the small difference between the gel fraction results obtained from hydrogels prepared with two different polymers, the results of the swelling kinetics are quite different as can be seen in Fig. 2.

The profiles of the swelling kinetics curves of the hydrogels (Fig. 2) indicate that PVA hydrogel offers a lower degree of swelling than PVP hydrogel does, although the concentration of the former is higher than that of the latter. For PVA hydrogel the equilibrium swelling was obtained after 8 h, with a degree of swelling only ca. 28%, whereas for PVP hydrogel it was observed that, after 20 minutes of immersion in water, a ca. 32% degree of swelling was attained; after 8 h, the hydrogel swelled 100%, and after 72 h, the equilibrium swelling was reached to the level of 150%.

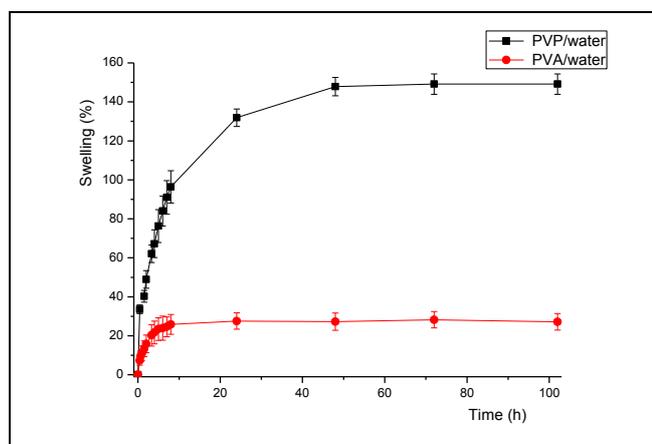


Figure 2: Kinetics of swelling of PVP and PVA hydrogel synthesized with nanocrystalline silver

The results suggest that the differences observed are probably due to a higher crosslinking density of the PVA hydrogel, encompassing crosslinking induced by gamma-radiation and physical crosslinking from numerous remaining intermolecular hydrogen bonds in PVA, which make this polymer more crystalline and less hydrophilic. Furthermore, according to Lakouraj *et al.* (2005), the amorphous nature of PVP and its higher affinity for water makes network rich in PVP swelling to a greater extent. In summary, the two important parameters that domain the state of swelling of the hydrogel and that stand out are: the crosslinking density and the intermolecular interactions between the polymer segments and the solvent molecules (Peppas *et al.*, 2006). On the other hand, one of the important features in the swelling rate or kinetics of swelling is determined by the sample size, extent and type of porosity of the porous structure, which are influenced by crosslinking density and by other factors such as temperature and pH changes, as well. However, these two last factors were not evaluated during the process of the hydrogel swellings.

To prove the reduction of silver ion (Ag^+) to colloidal silver (Ag^0), UV-visible plasmonic bands of the two obtained hydrogels were observed and measured as shown in Fig. 3. The spectra show peaks centered at 402.9 nm for the PVA hydrogel and 404.8 nm for the PVP hydrogel, suggesting that there was a reduction of Ag^+ to Ag^0 , and confirming the formation *in situ* of AgNPs. The wavelengths at which the two peaks were observed in the UV-visible spectra are characteristic for AgNPs with spherical shape according to the study by Mock *et al.* (2002). Although there is only a small offset between the two peaks of the plasmonic bands, one observes very similar profiles of the two curves indicating a very similar distribution of the sizes of the nanoparticles formed in the two hydrogels.

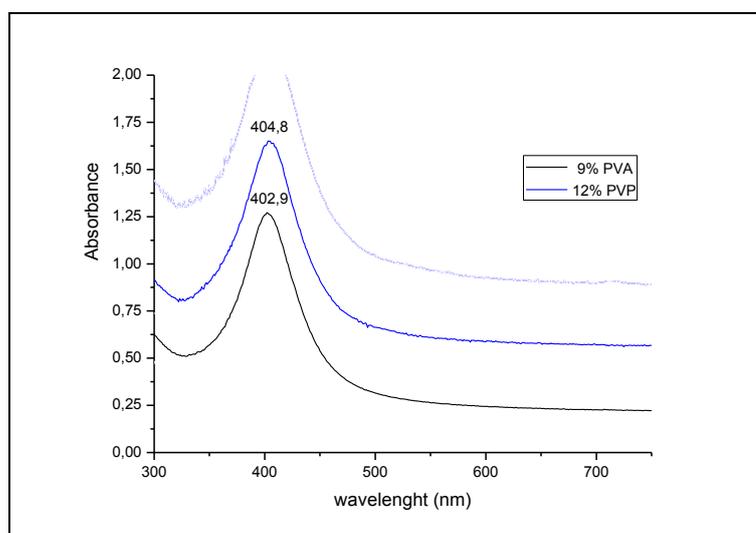


Figure 3: Plasmon resonance spectra obtained for the synthesized hydrogels.

Fig. 4 exhibits the results of tensile strength at break obtained for hydrogels synthesized with AgNPs. The highest stress values were obtained for the samples of PVA hydrogels, whereas the highest ones of elongation for samples of PVP, indicating that the resistance of PVA hydrogel with AgNPs is about 300% greater than that of PVA hydrogel, however, its elongation at break approximately 50% lower than that of the PVP hydrogel.

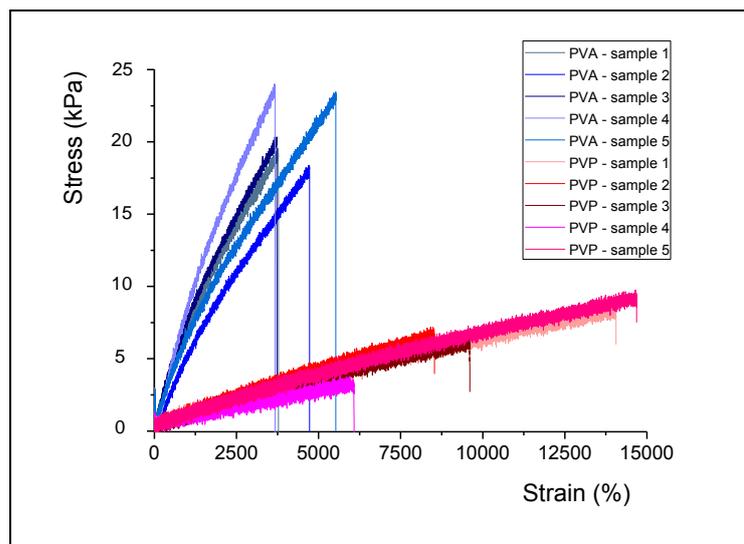


Figure 4: Diagram stress x strain obtained in the tensile tests of PVA and PVA hydrogels, both with nanocrystalline silver.

Thus, the results of tensile tests obtained for the two hydrogels synthesized with AgNPs corroborate with their results of swelling and gel fraction, which suggest a higher crosslinking density of the PVA hydrogel. Various interfering factors, inherent in the mechanical behavior of a polymer, mainly are due to its degree of crosslinking (Kudela, 1987).

Despite the differences obtained in tests of swelling, stress and strain of PVA and PVP hydrogels with different polymer concentrations, indicating different levels of crosslinking of two polymers, the results from spectra of plasmon resonance presented no significant changes in nanoparticles formed in relation to their size distribution.

4. CONCLUSIONS

Although the PVA hydrogel was synthesized with polymer concentration lower than that of the PVP hydrogel, the tensile test results of the first are higher than those of the second one. Nevertheless, its degree of swelling and elongation at break showed results with lower values than those obtained from the PVP hydrogel.

Despite the differences found between the physicochemical and mechanical properties of both hydrogels, their plasmon resonance spectra confirmed the synthesis of AgNPs *in situ* with spherical shape and with insignificant differences in the peak and size distribution of the nanoparticles. This study is being continued in order to obtain more complete information.

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