AQUEOUS SYNTHESIS OF PAAm/PVA/Ag NANOHYDROGELS

M. C. Hernández[a]*, C. Rojas[b], P. Estévez[c] and N. Bandres[c]

[a] Departamento de Física, Universidad Simón Bolívar, Caracas, Venezuela.
[b] Escuela de Física, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela.
[c] Departamento de Ciencia de los Materiales, Universidad Simón Bolívar, Caracas, Venezuela

*Corresponding author, E-mail: mahernan@usb.ve.

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ABSTRACT

In this work a novel synthesis methodology in aqueous medium of semi-interpenetrated nanohydrogels (HGNCs), of polyacrylamide (PAAm) with polyvinyl alcohol (PVA) and silver nanoparticles (AgNPs) is presented. The synthesis of the HGNCs/AgNPs was carried out in two phases: in a first stage, the AgNPs were obtained using the polyol method with PVA as a reducing agent and stabilizer of the metal nanoparticles, and in a second stage, the hydrogel semi IPN PAAm/PVA/AgNPs was synthesized in situ. A weight ratio of 2:1 PVA:AgNO3 and 4:1 PAAm:PVA is used. To evaluate the quality of the HGNCs/AgNPs obtained, the morphological and swelling properties of PAAm and PAAm/PVA blank samples are also analyzed. The dispersion in the polymer matrix, polydispersity and particle size of the metallic nanophase is evaluated through Transmission Electron Microscopy (TEM). The structure and pore size of the synthesized hydrogels are analyzed by Scanning Electron Microscopy (SEM) from lyophilized samples.

Keywords: metal-nanoparticles, polyol-synthesis, semi IPN hydrogel, morphologic-characterization.

SÍNTESIS ACUOSA DE PAAM/PVA/AG NANOHIDROGELES

RESUMEN

En este trabajo se presenta una metodología novedosa de síntesis en medio acuoso de nanohidrogeles semi-interpenetrados (HGNCs), de poliacrilamida (PAAm) con alcohol polivinílico (PVA) y nanopartículas de plata (AgNPs). La síntesis de los HGNCs/AgNPs se realizó en dos fases: en una primera etapa se obtienen las AgNPs utilizando el método del poliol con el PVA como agente reductor y estabilizante de las nanopartículas metálicas, y en una segunda etapa se sintetiza *in situ* el hidrogel semi IPN PAAm/PVA/AgNPs. Se utiliza una relación en peso 2:1 PVA:$AgNO_3$ y 4:1 PAAm:PVA. Para evaluar la calidad del HGNCs/AgNPs obtenido, se analizan también las propiedades morfológicas y de hinchamiento de muestras blanco de PAAm y PAAm/PVA. La dispersión en la matriz polimérica, polidispersidad y tamaño de partícula de la nanofase metálica son evaluadas a través de Microscopia Electrónica de Transmisión (MET). La estructura y tamaño de poros de los hidrogeles sintetizados son analizados por Microscopía Electrónica de Barrido (MEB) a partir de muestras liofilizadas.

Palabras claves: nanopartículas metálicas, síntesis de poliol, hidrogeles semi-interpenetrados, caracterización morfológica.

INTRODUCTION

Hydrogels are three-dimensional polymeric networks, characterized by their ability to absorb and/or release large amounts of water reversibly without affecting the mechanical stability of the material [1]. Its water absorption capacity is related to the level of cross-linking obtained in the synthesis process and is characterized by the degree of swelling of the material. This swelling occurs when the dry hydrogel (xerogel) begins to hydrate, allowing water molecules to enter the polymer network and increasing its volume. Water molecules interact with polar and hydrophilic groups through the formation of hydrogen bonds and the final level of hydration of the gel is obtained when a balance is reached between the osmotic forces, responsible for the diffusion of water into the material, and the cohesive forces, generated by cross-linking, which oppose the expansion and deformation of the polymer network. Semi-interpenetrated hydrogels (semi-IPN) are hydrogels in which one of the constituent components is cross-linked, while the other is a linear polymer. This type of hydrogels allows the properties of the two components to be combined and presents excellent behavior in terms of porosity, elasticity, mechanical resistance and degree of swelling. Recently, a marked interest has emerged in the use of hydrogels as a support matrix and for the stabilization of inorganic nanostructures such as metallic nanoparticles, nanoclays, carbon nanotubes, etc. [2]. The use of organic matrices, nanostructured in nature, combined with an inorganic phase at a nano scale, allows the development of materials with novel properties and a wide possibility of applications in areas such as: pharmacology, tissue support and growth, electronics, ecosystem remediation, catalysts, etc [3].

Particularly interesting is the development of hydrogels with silver nanoparticles, which stand out for their various applications in biology and medicine due to the bactericidal and fungicidal properties of silver [4][5].

Among the synthesis routes for metal nanoparticles are chemical methods, which allow controlling the size and shape of the nanoparticles [6][7]. Among them, the polyol method stands out, which is characterized by generating nanoparticles with different geometries, depending on the type of precursor metal, reaction conditions, and choice of the type of reducing and stabilizing agent [8].

Polyvinyl alcohol (PVA) is a highly polar, water-soluble and biodegradable polymer. It has hydroxyl groups in its structure, capable of forming chelates with the metal ions present in the aqueous solution and driving growth from Ag^+ ions to form atoms of metallic silver Ag^0 [9]. The interaction between the PVA chains and the metal aggregates generates a structure where the polymer chains limit the size of the synthesized nanoparticles, preventing the formation of agglomerates through steric hindrance [10].

The synthesis of nanohydrogels has been developed through numerous methods, of which the *in situ* polymerization of monomers stands out in the presence of an aqueous solution of previously formed nanoparticles. However, this methodology usually generates a low degree of cross-linking, in addition to requiring the presence of an external chemical reducing agent to obtain metallic nanoparticles [11]. The development of a synthesis route through in situ gelation of hydrogels in the presence of an aqueous solution of metal nanoparticles stabilized with PVA, represents a new approach for the generation of nanostructured materials.

In this work, a novel synthesis methodology in aqueous medium of semi-interpenetrated nanohydrogels (HGNCs), of polyacrylamide (PAAm) with polyvinyl alcohol (PVA) and silver nanoparticles (AgNPs) is presented. To evaluate the quality of the HGNCs/AgNPs obtained, the morphological and swelling properties of PAAm and PAAm/PVA blank samples are also analyzed. The dispersion in the polymer matrix, polydispersity and particle size of the metallic nanophase are evaluated through Transmission Electron Microscopy (TEM). The structure and pore size of the synthesized hydrogels are analyzed by Scanning Electron Microscopy (SEM) from lyophilized samples.

MATERIALS AND METHODS

The synthesis of the HGNCs/AgNPs was carried out in two phases: in a first stage, the AgNPs were obtained using the polyol method with PVA as a reducing agent and stabilizer of the metal nanoparticles, and in a second stage, the Semi IPN PAAm/PVA/AgNPs was synthesized *in situ*. A weight ratio of 2:1 PVA:$AgNO_3$ and 4:1 PAAm:PVA was used

Initially, two separate solutions were prepared, one containing the corresponding mass of PVA diluted in deionized water and another with the amount of $AgNO_3$ also diluted in deionized water. Both solutions were placed in an ultrasonic and heating protocol and after this the $AgNO_3$ solution was added to the PVA solution and heated with magnetic stirring, in order to obtain the aqueous dispersion of AgNPs.

The second phase consisted of the *in situ* polymerization of the semi-interpenetrated hydrogels, adding the acrylamide (AAm) and of N´N´ methylene bisacrylamide (N'N'MBA) to the aqueous dispersion of AgNPs from the previous step. On the other hand, gelation was achieved by adding a solution composed of potassium persulfate (KPS) in deionized water. The resulting hydrogel was washed in distilled water for 24 hours.

Swelling studies

The swelling phenomenon and its kinetics in nanocomposite materials were studied. To do this, the hydrogels were cut into disks of equal size and subjected to a drying process at room temperature for 7 days, followed by vacuum dehydration for 24 hours. Once the xerogels were obtained, the gravimetric test was carried out in distilled water at room temperature, which consisted of periodic weight records during certain intervals of time until reaching equilibrium, through the use of an analytical balance with an appreciation of 0.001g. To evaluate swelling and hydration phenomena

the absorption isotherms corresponding to the swelling percentage (%Ht):

$$\%Ht = \frac{m_t - m_0}{m_0}$$

and the hydration percentage %Wt:

$$\%Wt = \frac{m_t - m_0}{m_t}$$

were carried out.

Transmission Electron Microscopy (TEM)

The shape, particle size and dispersion of the silver nanoparticles were determined using a FEI Tecnai G2 Spirit transmission electron microscope operated at 100 kV. The samples were cut into thin sections using a LEICA–ULTRACUT UC7 ultramicrotome. Each sample was placed on a collodion/carbon supported copper grid. Histograms of the particle size distribution of the AgNPs were calculated from the TEM images by measuring the radii of all visible particles using the Digimizer 3.0 software.

Scanning Electron Microscopy (SEM)

The morphology of the synthesized hydrogels was evaluated by Scanning Electron Microscopy. For this, a treatment was previously carried out on the samples of the swollen hydrogels in a FreeZone lyophilizer model 7670521 brand LABCONCO until obtaining a porous material. Samples were coated with a thin platinum film using a magnetron sputter coater and then were evaluated in a FEI Quanta 250 FEG scanning electron microscope operated at 20 kV.

RESULTS AND DISCUSSION

Figure 1 compares the hydrogels synthesized in xerogel (left) and fully hydrated conditions (right).

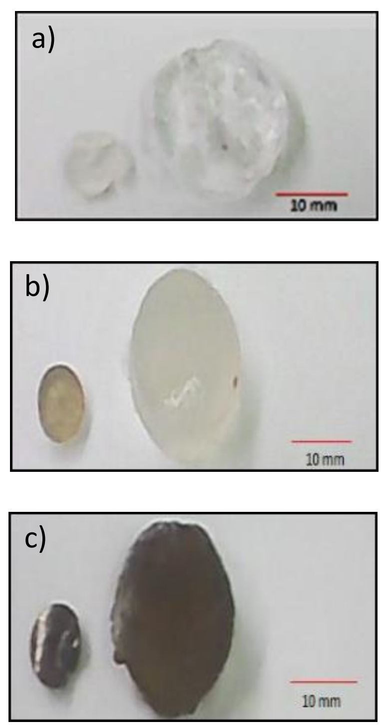
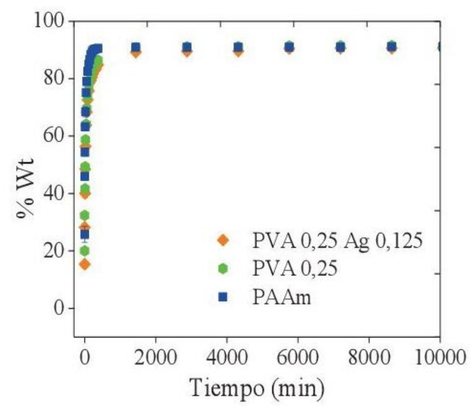


Fig. 1. Hydrogels in xerogel condition (left) and fully swollen (right): a) PAAm; b) PAAm/PVA; c) PAAm/PVA/AgNPs

Apparently it can be stated that the presence of the linear polymer (PVA) and/or the metallic nanophase (AgNPs) do not affect the swelling of the PAAm network. The deep brown color of the sample (c) is due to the nanometer-scale dispersion of the silver particles.

To fully quantify this behavior, the swelling and hydration tests were carried out and the effect produced by the formation of the semi-interpenetrated network as well as the presence of the nanoparticles was evaluated. Figure 2 shows the swelling isotherms at room temperature: (a) adsorbed water (%Wt), and (b) swelling index (%Ht), as a function of time,

(a)



(b)

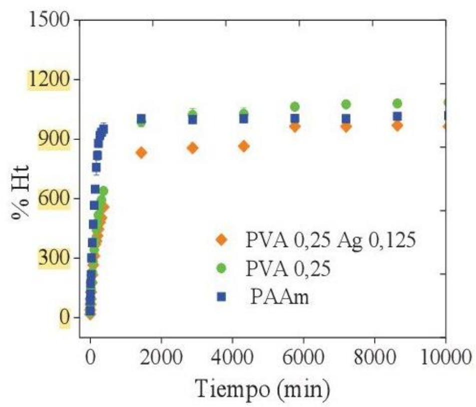


Fig. 2. Swelling isotherms as a function of time: a) adsorbed water b) swelling index

SEM micrographs of the lyophilized samples are presented in Figure 3. It is observed that the presence of the linear polymer reduces the size of the pores, from about 10 μm in the PAAm to about 3 μm in the sample with PVA and 0.7 μm for the nanohydrogel. This behavior can be explained as a consequence of the rigidity provided to the structure of the semi-IPN hydrogel by the presence of a semi-crystalline polymer

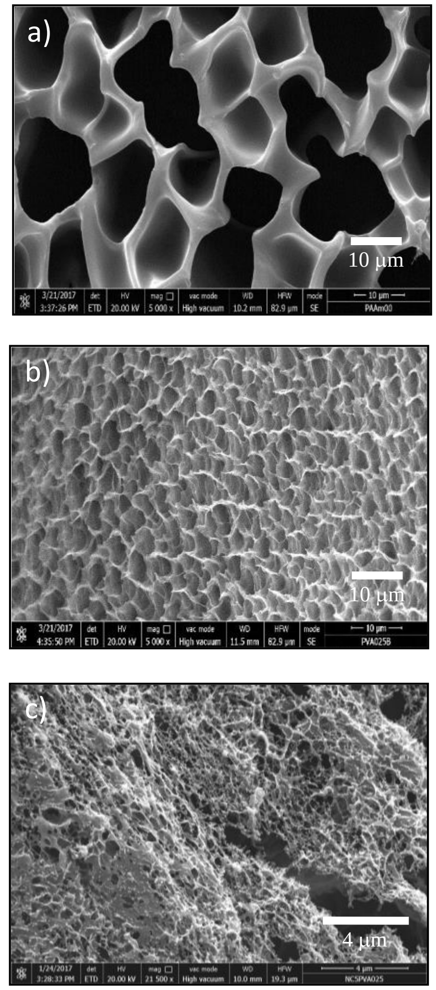


Fig. 3. SEM micrographs: a) PAAm; b) PAAm/PVA; c) PAAm/PVA/AgNPs

such as PVA. Figure 4a shows the TEM micrograph of the nanohydrogel. The presence of spherical silver nanoparticles with a uniform dispersion in the polymer matrix is observed. From the analysis of the size distribution of the nanoparticles, Figure 4b, an average radius of 9 nm and a relatively low polydispersity (9±4) nm are obtained. The results obtained by SEM demonstrate the formation of the three-dimensional network as well as the presence of defined pores. The morphological study by TEM on the nanohydrogel sample demonstrates the formation of an inorganic nanophase (AgNPs) with a narrow particle size distribution and uniform dispersion within the polymer matrix. The swelling and hydration characterization indicates that even though the pore size decreases with the inclusion of the linear polymer (PVA), as well as the silver nanoparticles, the Semi IPN samples obtained retain the swelling and water absorption properties of the PAAm hydrogel at equilibrium.

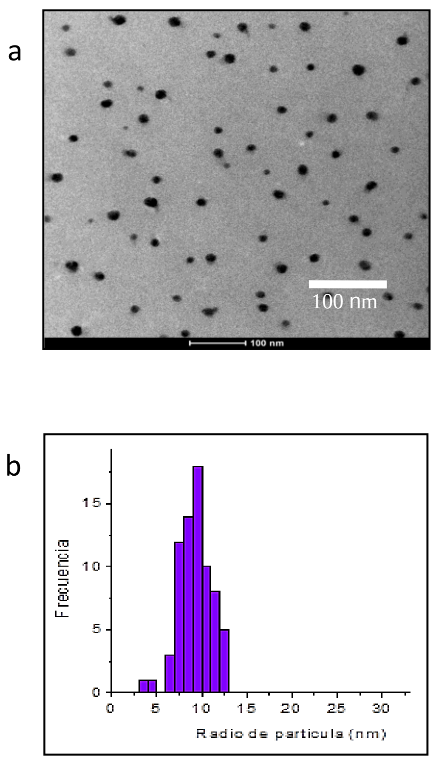


Fig. 4. a) TEM micrograph PAAm/PVA/AgNPs, b) AgNPs size distribution

It has been reported that the presence of the PVA is responsible for generating a greater number of hydrophilic and hydrophobic bonds with the PAAm chains, forming a more compact network that hinders water diffusion [12]. However, the presence of hydrophilic –OH groups in the PVA chain provides greater affinity with water [13]. This duality allows us to understand why, despite having a smaller pore size, the interpenetrated hydrogels retain the same water absorption capacity compared to the PAAm hydrogel.

CONCLUSIONS

It was possible to develop a methodology for the synthesis of nanohydrogels in aqueous solution using the polyol method. The morphological characterization by SEM of the synthesized hydrogels shows the formation of a three-dimensional network, as well as the presence of defined pores, for both the PVA/PAAm samples and the nanohydrogel. The morphological study by TEM of the silver nanophase demonstrates the formation of nanospheres with a narrow size dispersion and an uniform distribution in the polymer matrix. The swelling tests demonstrate that the incorporation of the linear polymer (PVA) and the silver nanophase do not affect the water absorption properties of the hydrogel.

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