SOME METHODS FOR DOPING POLY(VINYL ALCOHOL) HYDROGELS [PVA-HG]*

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Received December 21, 2004

This paper presents some new and ecological methods for doping PVA-HG with Cu\(^{2+}\) and with CuS. The methods for control of the PVA HG matrix loading with Cu\(^{2+}\) ions and CuS nanoparticles, the water absorption, the permittivity for Na\(^{+}\) ions, the chemical and thermal stability of the membranes obtained from these doped materials have been studied.

Key words: poly(vinyl alcohol), cryogel, copper ions, copper sulphide, water absorption, membrane permittivity.

1. INTRODUCTION

One of the goals of material research is to create new materials with properties tailored to a particular application and to understand the physical and chemical mechanisms that determine these properties. One of the newest methods to create such materials is doping of polymers with metals or salts.

A metal, in atomic or ionic state, introduced into a polymer matrix, generally improve the polymer behaviour and as a rule of composite materials, new properties, different of both matrix and filler ones, could be evidenced.

Poly(vinyl alcohol) is an important material in view of its large-scale applications, such as biomaterials, biosensors, electrochemical sensors, membranes with selective permittivity, viscous medium for controlling the crystallization process of salts, for controlled drug delivery or catalytic systems, etc. because it is a non-toxic, non-carcinogenic, biodegradable, biocompatible, water-soluble, and non-expensive polymer. It could be also matrix for metal ions or salts in ecological composites [1, 2].

The filler particles could be retained in the polymer matrix by physical and/or chemical bonds or by mechanical immobilization. The three dimensional polymer networks help in the mechanical immobilization of the filler.


Supplementary, the physical or chemical interaction between the polymer matrix and the filler lead to more stable composite systems. PVA fulfills all these requested conditions. It can react with different organic or inorganic substances, via -OH groups from its macromolecular chain, and three dimensional networks, which can absorb very high water amount (up to 1800%), could be obtained. The PVA curing could be made also by using physical methods such as irradiation with β, γ or X radiation or by applying repeated freezing-thawing cycles [3,4]. These networks are known as hydrogels [HG]. Hydrogels could be homogeneous or heterogeneous systems, depending on the applied method of HG-s obtaining. PVA HG-s could immobilize different fillers. The presence of the polar –OH groups permits also the physical interactions (by H-bonding or by van der Waals dipole-ion or dipole-dipole interactions) and chemical interactions (by complexing reactions) [1,2].

Because the presence of the transition metals ions and its sulphides in the polymer matrix lead to very interesting thermal and electrical properties of the composite material, a lot of recent researches were reported [5,6,7].

The PVA matrix was obtained by different curing ways. All of these methods have important disadvantages. The polymer γ-irradiation leads not only to the polymer curing, but also to its degradation. The polymer irradiation is a very difficult controlled technique for hydrogels obtaining [5]. This technique evidences a less reproducibility. Supplementary, by irradiation, new C-C bonds are formed and the biodegradability of the polymer decreases.

The PVA curing by chemical ways requests the chemical agents use. The last ones are usually toxic (di-aldehydes, di-halide derivatives of hydrocarbons), expensive, lead to non-biodegradable materials and the conditions of crosslinking reactions are usually difficult (high temperature, vacuum, long time) [7].

In this paper, we studied the doping of PVA-HG, obtained by repeated freezing-thawing technique, with copper ions and copper sulphide. This method for polymer matrix obtaining, avoids all the above mentioned drawbacks of the other methods. The control methods for the doping agent concentration in the polymer matrix were evidenced. The influence of the nature and filler concentration on some properties of the obtained composite materials such as, water absorption and membrane permittivity for the Na+ ions has been also studied.

2. EXPERIMENTAL DATA

2.1 THE OBTAINING OF THE PVA HG

PVA 90-98 (900 polymerization degree and 98% hydrolysis degree), industrial grades, without further purification have been used.

PVA has been solved in distilled water, at 80°C, under continuous stirring.
The resulted solution, with 14% solid content, has been introduced in PVC vials and kept for 12 hours at (-15°C) and then for 12 hours at room temperature (25°C). This cycle has been repeated for three times. A white, heterogeneous, porous membrane of hydrogel, thermo reversible, with a good mechanical resistance has been obtained. Figure 1 shows an image of the PVA hydrogel.

2.2 THE OBTAINING OF THE COMPLEXED PVA HG-Cu²⁺

Round samples from the PVA-HG membrane, with 1 cm diameter, have been immersed in aqueous solutions of [Cu(NH₃)₄]SO₄, with different concentrations, at a pH between 8-12, and kept for 48 hours to attain the chemical equilibrium. A green complex PVA-Cu²⁺ has been obtained, as it can be seen in Figure 2.

2.3 THE OBTAINING OF THE PVA HG-CuS NANO-COMPOSITE

Then, round samples cut off from the complexed PVA membrane have been immersed in solutions of (NH₄)₂S, with different concentrations, between 10⁻³-14x10⁻³ mol/L, and kept 24 hours to attain the chemical equilibrium.

The membrane colour turned to black, due to CuS particles formed in the hydrogel matrix. Because the Cu²⁺ ions are separately disposed in the polymer matrix, the resulted CuS particles are very finely dispersed and well fixed in the polymer matrix. An image of the PVA membrane doped with very fine particles of CuS can be seen in Figure 3.

Fig. 1 – Photographic image of the PVA hydrogel membrane.
2.4. METHOD FOR THE DETERMINATION OF THE Cu\textsuperscript{2+} REPARTITION CONSTANT, $K_{Cu}^{2+}$

The repartition of the Cu\textsuperscript{2+} ions between the aqueous solution and PVA hydrogel has been determined by a spectrophotometric method, using the correlation between the solution extinction at 600 nm and its concentration.
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(Guretki I. et al., 1992). From the value of the initial solution concentration and that of the concentration of the solution in which the hydrogel sample has been immersed for 48 hours, the amount of copper ions from the hydrogel has been calculated. This quantity has been divided by the hydrogel volume, determined by measuring the volume of a liquid displaced by the sample. The concentration of the copper ions in the hydrogel, expressed in mg Cu^{2+}/L, has been calculated. The ratio between the concentration of the Cu^{2+} ions in the hydrogel and that in the aqueous solution, named repartition constant K_{Cu^{2+}}, has been calculated.

2.5. METHOD FOR THE DETERMINATION OF THE S^{2-} REPARTITION CONSTANT, K_{S^{2-}}

The concentration of the S^{2-} ions in the initial solution and in the solution in which the complexed hydrogel has been immersed, has been determined by a volumetric method (Liteanu C., 1972). The initial mixture formed by: 5 mL of (NH₄)₂S aqueous solution, 5 ml of 1N acetic acid solution and 10 ml of I₂/I⁻ solution (0.1N), has been kept for 10 minutes in the dark and then has been titrated with a 0.1N Na₂S₂O₃ aqueous solution.

The following reactions took place:

\[(\text{NH}_4)_2\text{S} + \text{I}_2 = 2\text{NH}_4\text{I} + \text{S}\]
\[\text{I}_2 \text{ excess} + 2\text{Na}_2\text{S}_2\text{O}_3 = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6\]

The differences between the amount of iodine introduced in the mixture and the amount of the iodine in excess represents the iodine reacted with sulphide ions.

The repartition constant of the sulphide ions between the hydrogel and the aqueous solution has been calculated.

2.6. SOLID CONTENT DETERMINATION

All the obtained materials (PVA HG, PVA HG-Cu^{2+} and PVA HG-CuS) have been kept immersed in distilled water and have been attained the swollen equilibrium. The solid content of the obtained materials in swollen state has been determined by cutting out of the cylindrical samples (diameter: 1.77–1.80 cm, high: 0.5–0.6 cm, weight: 1.7–2.0 g), weighing, keeping them in a thermosetting oven at 105°C for 5 hours and weighing the dried samples.

The solid content of the material has been calculated with the following formula:

\[\text{CS(\%)} = \frac{m_f}{m_i} \times 100\]  \hspace{1cm} (1)
where: \( m_f \) is the weight of the sample in the swollen state (g) and \( m_i \) is the sample weight in the dried state (g).

### 2.7. WATER ABSORPTION CALCULATION

The sample water absorption has been calculated with the following formula:

\[
H_2O(\%) = \frac{100(100 - CS)}{CS} \tag{2}
\]

where: \( H_2O(\%) \) is the percent of water absorbed and \( CS \) is the solid content of the material expressed in percents.

### 2.8. DETERMINATION OF THE MEMBRANE PERMITTIVITY FOR Na\(^+\) IONS

A diffusion cell with two compartments separated by the tested membrane, with an active surface by 9.62 cm\(^2\) was used to study the diffusion of Na\(^+\) through PVA HG, PVA HG-Cu\(^{2+}\) and PVA HG-CuS membranes.

Each diffusion cell compartment has 250 ml capacity.

To study the diffusion process through membranes, in one compartment was introduced the salt solution (NaCl, 0.1 N) and in the other, distilled water.

The diffusion was studied by measure the variation of the Na\(^+\) ions concentration in the distilled water compartment versus the time.

To determine the Na\(^+\) concentration, a flam-photometric method has been used (Flapho 4).

The membrane permittivity has been calculated with the following formula:

\[
P = \frac{c_{\text{dif.}}l}{S.t.C_A} \tag{3}
\]

where: \( c_{\text{dif.}} \) is the concentration of the Na\(^+\) diffused through the membrane. It was determined by flam-photometry; \( l \) is the membrane thickness (m); it has been measured with a micrometer; \( S \) is the membrane surface active for the diffusion process (m\(^2\)); \( t \) is the time at which the diffused ions concentration has been measured (s); \( C_A \) is the initial salt concentration in the salt solution compartment (mval/m\(^3\)).

### 3. RESULTS AND DISCUSSION

Tables 1 and 2 present the experimental data and the values of the repartition constants of Cu\(^{2+}\) ions and the sulphide ions between the hydrogel and the aqueous solutions.
Table 1

Experimental data for the repartition of the copper ions between the hydrogel and the aqueous solution of [Cu(NH₃)₄]SO₄.

<table>
<thead>
<tr>
<th>Nr. Crt</th>
<th>Initial solution</th>
<th>Final solution (after 48 hours of HG immersion)</th>
<th>M_{\text{absorbed}} \text{Cu}^{2+} (mg)</th>
<th>V_{\text{HG}} (mL)</th>
<th>K</th>
<th>$K_{\text{Cu}^{2+}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_{\text{in. sol.}} (mg Cu²⁺/L)</td>
<td>C_{\text{fin. sol.}} (mg Cu²⁺/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4020.21</td>
<td>3327.07</td>
<td>13.86</td>
<td>0.30</td>
<td>13.89</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6815.88</td>
<td>5637.54</td>
<td>23.56</td>
<td>0.32</td>
<td>13.06</td>
<td>13.45</td>
</tr>
<tr>
<td>3</td>
<td>10235.37</td>
<td>9057.03</td>
<td>23.56</td>
<td>0.195</td>
<td>13.34</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>13724.18</td>
<td>11875.81</td>
<td>36.96</td>
<td>0.23</td>
<td>13.53</td>
<td></td>
</tr>
</tbody>
</table>

From the Table 1, it can be noticed that the copper ions which react with the PVA HG membrane have been concentrated 14-th times in the membrane by compare with the Cu²⁺ concentration in the aqueous solution.

Table 2

Experimental data for the repartition of the S²⁻ ions between the complexed hydrogel and the aqueous solution of (NH₄)₂S.

<table>
<thead>
<tr>
<th>Nr,crt</th>
<th>Conc. of initial S²⁻ sol. (10⁻³M)</th>
<th>$\frac{m_{\text{S}²⁻}(10^{-3} \text{g})}{m_{\text{HG}}(\text{g})}$</th>
<th>$\frac{m_{\text{S}²⁻}(10^{-3} \text{g})}{m_{\text{sol.}}(\text{g})}$</th>
<th>K</th>
<th>$K_{\text{S}²⁻}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>5.2879</td>
<td>0.2692</td>
<td>19.6430</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>3.858</td>
<td>0.3334</td>
<td>11.5717</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>4.3827</td>
<td>0.359</td>
<td>12.208</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>5.1197</td>
<td>0.3462</td>
<td>14.7882</td>
<td>13.64</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>5.8223</td>
<td>0.3718</td>
<td>15.6597</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>12</td>
<td>5.429</td>
<td>0.4360</td>
<td>12.4518</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>13</td>
<td>4.2156</td>
<td>0.4616</td>
<td>9.1325</td>
<td></td>
</tr>
</tbody>
</table>

From the Table 1, it can be noticed that the copper ions which react with the PVA HG membrane have been concentrated 14-th times in the membrane by compare with the Cu²⁺ concentration in the aqueous solution.

From the Table 2 it can be seen that the S²⁻ ions react stoechiometrically with the Cu²⁺ from the membrane and as consequence, its repartition constant is also approximately 14.

The amount of the Cu²⁺ and CuS introduced in the PVA HG membrane, could be controlled by the concentration of the immersion solution of [Cu(NH₃)₄]SO₄ and (NH₄)₂S, respectively, taking also into account the value of the
determined repartition constant. The PVA HG membranes have been loaded with CuS up to 10% by weight.

**Table 3**

<table>
<thead>
<tr>
<th>Type of material</th>
<th>CS (%)</th>
<th>H₂O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA 90-98 HG</td>
<td>17.15</td>
<td>608.15</td>
</tr>
<tr>
<td>PVA 90-98 HG-Cu²⁺</td>
<td>15.86</td>
<td>530.40</td>
</tr>
<tr>
<td>PVA 90-98 HG-CuS</td>
<td>6.68</td>
<td>1397.30</td>
</tr>
</tbody>
</table>

It can be noticed, from the Table 3, that the equilibrium water content of the complexed PVA HG sample decreased by compare with the initial PVA HG sample. This aspect could be explained by the increasing of the polymer crosslinking number, due to the complexation reaction, as it is represented by the following chemical equation:

\[
\text{CH}_2\text{CHCH}_2\text{OH} + \text{Cu}^{2+} \rightarrow \text{CH}_2\text{CH}\text{Cu}\text{CH}_2\text{OH}
\]

The dramatic increase of the equilibrium water content of the PVA HG-CuS composite material, compared with PVA HG and PVA HG-Cu²⁺, could be explained by the reaction of the Cu²⁺ ions with the S²⁻ ions. As consequence of this chemical reaction, the chemical bonds between Cu²⁺ ions and polymer chains have been broken, the number of the polymer crosslinking decreased and the nanometric particles of CuS very finely dispersed in the hydrogel matrix acted as chain spacers. This process could be represented by the following chemical reaction:

\[
\text{CH}_2\text{H} + \text{CuS} \rightarrow \text{CuSS} \rightarrow \text{CH}_2\text{CHCH}_2\text{OH}
\]

Another evidence of this mechanism of reaction is the value obtained for the membranes permittivity for the Na⁺ ions.
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### Table 4

The membranes permittivity for the Na<sup>+</sup> ions.

<table>
<thead>
<tr>
<th>Type of material</th>
<th>P (10&lt;sup&gt;-9&lt;/sup&gt; m&lt;sup&gt;2&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA 90-98 HG</td>
<td>6.106</td>
</tr>
<tr>
<td>PVA 90-98 HG-Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>5.450</td>
</tr>
<tr>
<td>PVA 90-98 HG-CuS</td>
<td>6.912</td>
</tr>
</tbody>
</table>

A more swollen polymer network, with a decreased crosslinkings number compared to the complexed PVA HG –Cu<sup>2+</sup> and higher pores dimensions, due to the presence of the CuS nanoparticles among the polymer chains, determines higher membrane permittivity of the composite membrane PVA HG-CuS against the Na<sup>+</sup> ions.

The above mentioned mechanism of PVA HG-Cu<sup>2+</sup> and PVA HG CuS membranes formation is supported also by the materials heat resistance modifications. So, the initial PVA HG is thermo-reversible. By heating the membrane immersed in water, at more than 60ºC, it begins to solve.

By complexing the hydrogel with Cu<sup>2+</sup>, because of the formation of the supplementary crosslinkings, the complex becomes heat resistant. It could be boiled in water, without dissolution.

When the copper ions from the PVA HG complex react with the sulphide ions, the crosslinkings, due to the copper ions bounded by different polymer chains, broken up and the PVA HG-CuS composite becomes again thermo reversible. By heating it, the fine particles of CuS have been delivered and then, the PVA HG has been solved.

### 4. CONCLUSION

A new and ecological method for doping PVA with copper ions and nanoparticles of copper sulphide was described.

This method avoids the degradation of the polymer that takes place in the process of polymer crosslinking by gamma or X- irradiation and avoids the use of the toxic crosslinkers, organic solvents, high temperature, vacuum and long reaction time.

The high water sensitivity of the PVA HG-CuS nano-composite material and the semi-conductive properties of the sulphides, make it suitable as moisture sensor.

The properties of the composite material depend on the amount of the filler. This one could be controlled by the concentration of the solution of [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub> and/or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and taking into account the value of the determined repartition constants K<sub>Cu<sup>2+</sup></sub> and K<sub>S<sup>2-</sup></sub>, respectively.
A correlation between the reaction mechanism of PVA HG with copper ions and sulphide ions, and the water absorption capacity, thermal stability and permittivity of the membranes was made.

REFERENCES