

Hybrid Hydrogel Materials with Incorporated Nanoparticles

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Synthesis and physico-chemical studies of new promising hybrid hydrogels based on polyvinyl alcohol (PVA) acetates and copolymer hydrogels based on vinyl monomers have been studied. Acrylamide and Acrylonitrile were used as some of components that carry various fillers. Sponge acetates of polyvinyl alcohol were used as enforcing net. The synthesized composites demonstrated high strength as compared to standard hydrogels. Yung-module varied in the range of 80 to 300 kPa depending on the extent of PVA acetate matrix filling with hydrogel component. The materials showed high sorbability to water and water solutions. Study of swelling kinetics as compared to solvents of various nature (water, ethanol, sunflower oil) was carried out.

Keywords: Hydrogels, Polymer Composites, Nanocomposites.

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1. INTRODUCTION

Polymeric hydrogels are three-dimensional high-molecular networks containing physically or chemically cross-linked (co)polymeric chains and water. Due to their high biocompatibility and the ability to incorporate drugs into their composition, the hydrogels are widely used in medicine [1], pharmacology, and biology to develop various biomaterials, such as implants, soft contact lenses, wound coatings, cell carriers, drug delivery systems (e.g. that of heparin) [2], etc. Hydrogels are most widely used in regenerative medicine [3] as tissue barriers, bioadhesives, and drug depots, to deliver bioactive agents to boost natural regeneration processes, as well as for the encapsulation and cell delivery.

Hybrid polymer materials based on polyvinylalcoholacetates and copolymer hydrogels based on acrylic monomers (acrylamide, acrylonitrile, acrylic acid, isopropylacrylamide, etc) have been synthesized. These materials have greater strength and higher sorbability in comparison to solvents of various nature and polarity (water, physiological solution, petroleum, hexane, sunflower oil, etc).

2. MATERIALS AND METHODS

2.1 Materials

Following materials were used to synthesize polymer hydrogels and composite based on them: Formaldehyde 35%, polyvinyl alcohol ("Applichem" GmBH 95%) molecular mass 7200), acrylonitrile (distilled), Acrylamide (Merck>99.9%) N,N-methylenebisacrylamide (Merck 98%).

2.2 Methods

Polyvinyl alcohol acetate net was obtained by means of crosslinking PVA (polyvinyl alcohol) using formalde-

hyde. Interpenetrated nets were obtained in water by swelling acetate net in an acrylic matrix. The acrylic matrix was immobilized in acetate net by radical polymerization of acrylic monomers with a cross-linking agent N,N-methylene-bis-acrylamide with a redox system based on potassium persulphate and sodium metha-bisulphate.

The obtained composite materials were characterized using swelling in water, alcohol and oil. Micro- and macro-photos were taken as will. Yung-modul was found with the help was found with the help of universal deformation device MPK-1, x-ray-fluorescence spectrometer Elvax Light SDD.

3. RESULTS AND DISCUSSION

Due to interpenetrating system of open pores (Fig. 1) the obtained materials have higher speed of absorption of the mentioned solvents, for instance, the swelling degree in water reached in 10 sec. constitutes from 2.5 to 6.7 g/g (Fig. 2) Equilibrium degree of swelling of the synthesized sponge materials was determined gravimetrically and constituted from 5 to 22 g/g (in water), from 4 – 18 g/g (in sunflower oil) and 5 – 22 (in ethanol), depending on chemical composition.

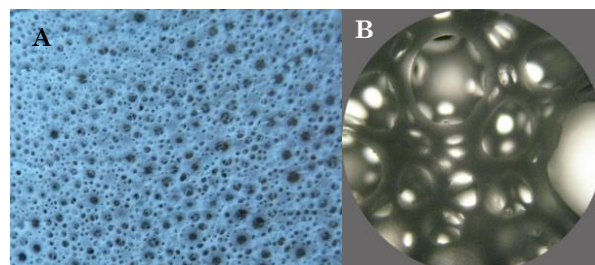


Fig. 1 – The enforcing net based on PVC acetal a) macro-photography; b) microphotography;

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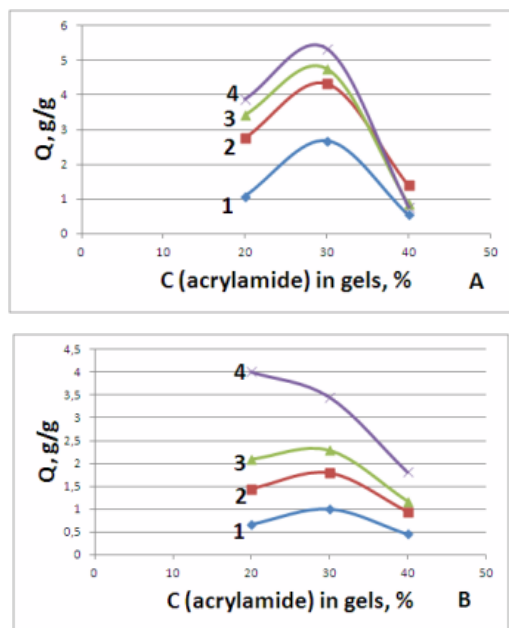


Fig. 2 – Swelling a) composite, b) pure gels; 1.2.3.4 – 5, 30, 60, min and 24 hours, respectively;

The influence of prior wetting of an enforcing net of (PVA) acetal by a "good" solvent (water) was investigated. With this aim the enforcing net was swollen to an equilibrium state followed by squeezing. Fig. 3a shows that priory wetted net reached equilibrium swelling much quicker. It means that taking into account polymerization time, hemo (about 10 min.) is significant since a gel has enough time to uniformly spread in the enforcing net prior to polymerization. It should be mentioned that the net wetted in advance swells much better in "bad" solvents (Fig. 3b) and therefore introduction of hydrophobic materials in the composite might appear promising.

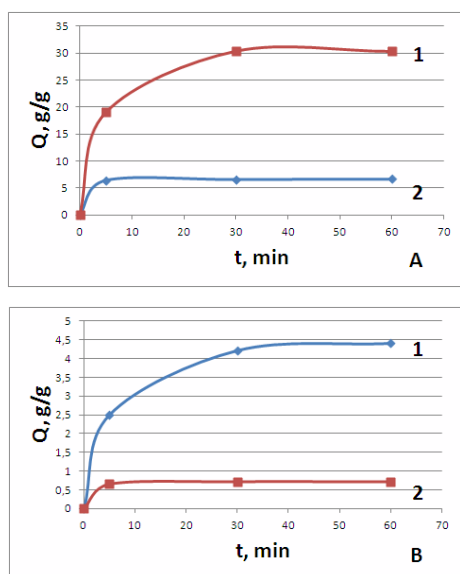


Fig. 3 – Swelling of wet and dry sponges; a – in water; b – in oil; 1 – wet sponges; 2 – dry sponges;

Testing of hydrogel composite mechanical properties was carried out with help of universal deformation

installation MPK-1. The test constituted in the sample squeezing at a constant speed of 0.25 mm/min. The testing process was written on a diagram stripe moving with the speed of 720 mm per hour. It was found that Yung module of synthesized hybrid materials varied from 80 to 300. KPA depending on the extent of filling of PVC acetal –based matrix with hydrogel component.

Relative elongation in this case varied in the range of 10% to 42%.

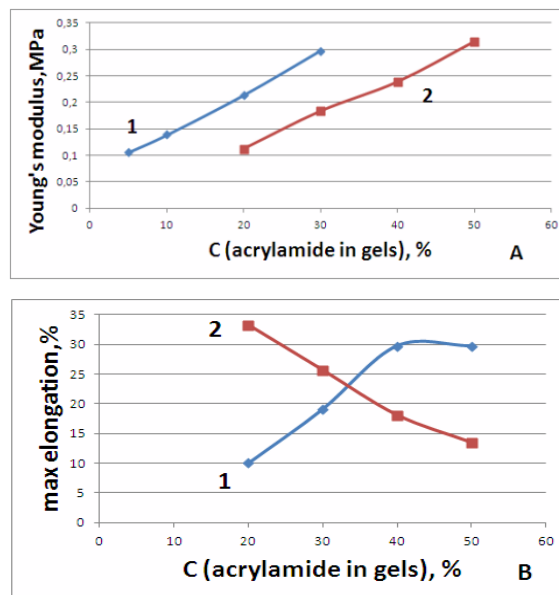


Fig. 4 – Dependences on monomer concentrations in the gel incorporated in the net (1), pure gel (2), a) Yung module, b) maximum elongation;

The studied materials are supposed to be used as carriers of various fillers, silver and magnetite particular [4, 5]. Therefore, concentrations of incorporated nanoparticles in gels were measured by X-ray fluorescence analysis.

Measurements were carried out using ElvaX spectrometer with the accuracy of metal mass fractions determination not less than 0.1%. Limits of heavy metal admixture determination in the matrix constituted 1 ppm.

Parameters of determination:

1. Current: about 50 mkm
2. Power: 40 kV
3. Time of exposition: 120 sec.
4. Filter of primary radiation: Ti

In case of nanogels containing Ag, studies showed that with the rise of the stated silver concentration increase of x-Ray fluorescence radiation is observed in the energy range of the specified element. Experimental data are given in Fig. 5a-b.

Somewhat different picture (Fig. 5c-d) is observed for Fe-containing nanogel samples. The rise of the stated content of iron cations to 0.75% is accompanied by more intensive x-ray fluorescence radiation in the energy range of the element, however, this dependence is not observed due to the material transition in the collapsed state in the process of swelling in the solution where iron salt concentration is > 1%.

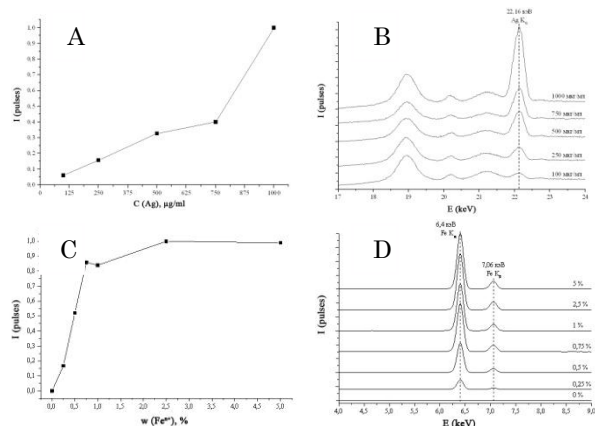


Fig. 5 – X-ray fluorescence radiation intensity versus concentration: a – Ag, c – Fe; X-ray fluorescence radiation intensity versus energy for nanogels containing b – Ag, d – Fe;

Currently silver is one of the most common fillers. Silver is a relatively non-toxic for human cells, but possesses antimicrobial properties against a wide range of bacterial strains. That is why silver in various forms such as elementary silver, silver ions, and silver nanoparticles are widely used for the manufacture of domestic, industrial and medical products [6-7].

Bactericidal properties of silver nanoparticles incorporated in hydrogel matrices towards gram-positive (*S. Aureus*) and gram-negative (*E. Coli*) microorganisms have been investigated.

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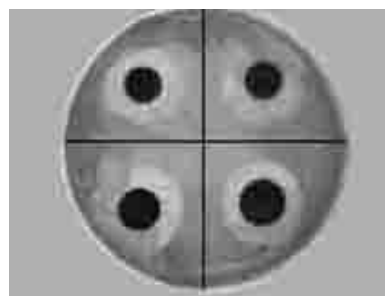


Fig. 6 – Test of inhibiting zones towards *S. Aureus*, 10^8 colonies of forming units;

4. CONCLUSIONS

Hybrid hydrogel composites were synthesized basing on PVS acetal and hydrogel copolymers of vinyl series. Silver and magnetite nanoparticles incorporation techniques into the synthesized polymer matrices have been developed. The nanoparticles content was studied by x-ray fluorescence analysis. Physico-chemistry properties (i.e. Yung module) of the synthesized composites as factor their swelling and elongation in various solvents were investigated. High anti-bacterial action of the synthesized nanocomposites containing silver towards gram-positive and gram-negative bacteria has been demonstrated.