PROCEEDINGS OF THE INTERNATIONAL CONFERENCE
NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **3** No 2, 02NNSA14(3pp) (2014)

pH-sensitive Hybrid Hydrogel Materials with Incorporated Nanoparticles

S.O. Kryklia[1,*], Yu.M. Samchenko[1,†], T.P. Poltoratska[1], V.V. Konovalova[2]

[1] *Ovcharenko Institute of Biocolloid Chemistry, National Academy of Sciences of Ukraine, 42, Vernadskogo Str., 03680 Kyiv, Ukraine*
[2] *National University "Kyiv-Mohyla Academy", 2, Skovorody Str., 04655 Kyiv, Ukraine*

(Received 20 July 2014; published online 29 August 2014)

Synthesis and physico-chemical studies of new promising hybrid hydrogels based on polyvinyl alcohol (PVA) acetales and copolymer hydrogels based on vinyl monomers have been studied. Acrylamide, N-Isopropylacrylamide and Acrylic acid were used as components of interpenetrating networks based on PVA acetals. Sponge acetales of polyvinyl alcohol were used as enforcing net. Study of swelling kinetics as compared to solvents of various nature (water in various pH, ethanol, toluene etc) was carried out. IR comparative spectra were obtained for different composites. High anti-bacterial action of the synthesized nanocomposites containing silver towards gram-positive and gram-negative bacteria has been demonstrated.

Keywords: Hydrogels, Polymer composites, Nanocomposites.

PACS number: 68.55. – am

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. Acetals of polyvinyl alcohol characterized by good mechanical properties [4], primarily due to the crystallites formed as a consequence of the action of Van-der-Waltz interactions. According to the data given in [5], depending on the method of preparation, the degree of crystallinity of PVA can reach 65%.

Hybrid polymer materials based on polyvini lalcohol acetales and copolymer hydrogels based on acrylic monomers (acrylamide, 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 in various pH, ethanol, toluene etc) and exhibit pH- and thermo-sensitive behavior.

2. MATERIALS AND METHODS

2.1 Materials

Following materials were used to synthesize polymer hydrogels and composite based on them: Formaldehyde 35%, polyvynil alcohol (“Applichem”GmBH 95%) molecular mass 7200), Acrylic acid, N-Isopropylacrylamide, Acrylamide (Merck>99.9%} N,N-methylenebicacrylamide (Merck 98%).

2.2 Methods

Polyvynil alcohol acetale net was obtained by means of crosslinking PVA (polyvynil alcohol) using formaldehyde. Interpenetrated nets were obtained in water by swelling acetale 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-acrylanide with a redox system based on potassium persulphate and sodium metha-bisulphate.

The obtained composite materials were characterized using swelling in water in varios pH, alcohol, toluene etc. Micro- and macro-photos were taken as will. IR comparative spectra were obtained for different composites.

3. RESULTS AND DISCUSSION

Polyvynil alcohol acetale net sponges was obtained in wide concentration range of PVA and formaline as shown in Table 1. Swelling of sponge synthetic material in a wide variety of solvents (water, etanol, toluene, etc.)

Table 1 – Enforcing net sponges synthesized from compositions with different concentrations of PVA and formaline;

Sponge №	PVA, wt%	Formaline, wt%
1	6,5%	7,5%
2	7,2%	8,2%
3	8%	7,2%
4	8%	9,4%
5	8%	5%
6	9,1%	8,3%
7	9,1%	10,8%
8	9,1%	5,8%
9	11%	9,9%
10	11%	12,9%
11	11%	6,9%
12	13%	11,7%
13	13%	15,2%
14	13%	8,2%

* sgamdev@gmail.com
† yu1sam@yahoo.com

Table 2 – Swelling rate (g/(g*s)) of some samples in water and ethanol;

Water			
Sponge №	2 min.	5 min.	30 min.
3	0,0652	0,0139	0,0019
6	0,0197	-0,0044	0,0005
9	0,0032	0,0007	0,0001
Ethanol			
Sponge №	2 min.	5 min.	30 min.
3	0,0074	0,0056	0,0015
6	0,0077	0,0091	0,0025
9	0,0035	0,0054	0,0004

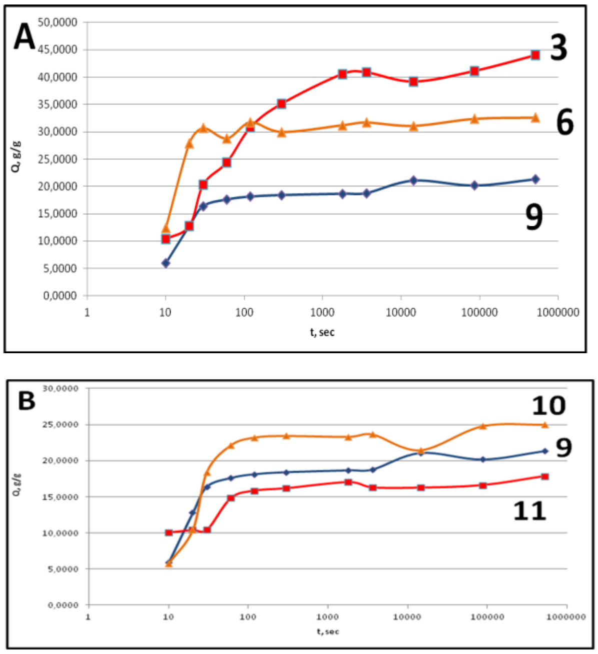

Fig. 1 – Effect of the concentration of: a – PVA, b – formaline, on the water swelling kinetics of sponges; 3,6,9,10,11 – sponge numbers in Table 1;

was investigated. Swelling rate of some samples in water and ethanol are shown in Table 2. Comparison of the kinetics of swelling of some samples depending on the concentration of PVA or formaline is shown in Fig.1a-b.

To apply the technique of obtaining interpenetrating networks, it is necessary to swell the sponge in the hydrogel-forming acrylic composition. Thus, depending on the concentration of the acrylic matrix, sponge can exhibit abnormal degree of swelling and becomes unfit for creating composites. Figure 2a-b shows photos of swollen sponge in acrylic matrices of various concentrations.

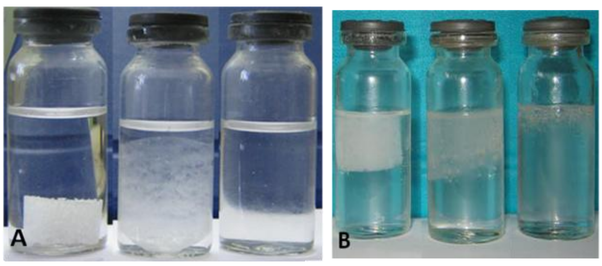

Fig. 2 – Swelling of sponges; a – from left to right increasing wt% of Acrylamide; b – from left to right increasing wt% of Acrylic acid;

A schematic process of formation of interpenetrating networks is shown in Fig. 3.

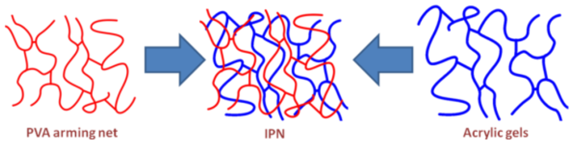

Fig. 3 – formation of interpenetrating networks (IPN);

Porosity can be controlled by varying amount of incorporated acrylic gel (Fig. 4).

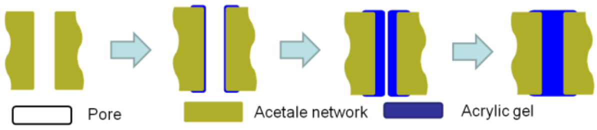

Fig. 4 – varying of porosity of interpenetrating networks;

IR comparative spectra obtained for different composites and for pure sponge shown in Fig. 5.

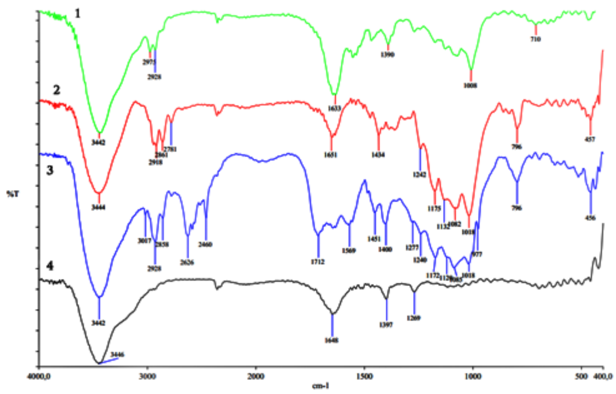

Fig. 5 – IR spectra: 1 – composite with N-Isopropylacrylamide, 2 – pure sponge, 3 – composite with Acrylic acid, 4 – composite with Acrylamide;

Study of swelling kinetics of obtained composites was carried out. Fig.6 shows that that a pure sponge (a) very quickly reaches equilibrium, while the composites based on Acrylamide (c) and Acrylic acid (b) swell slowly - this may be due to the fact that part of the pores has been closed by the acrylic gel component. With the time, composite based on Acrylic acid increases the degree of swelling, which is similar for pure Acrylic acid gels behavior.

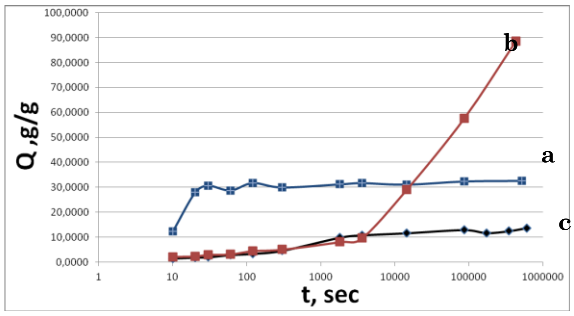

Fig. 6 – Swelling kinetics of: a – pure sponge № 6, b – composite based on Acrylic acid (80 wt% of acid), c – composite based on Acrylamide (80 wt% of acrylamide);

Composites based on acrylic acid showed pH-sensitivity properties (Fig.7). Difference of swelling degrees at different pH values can vary tenfold.

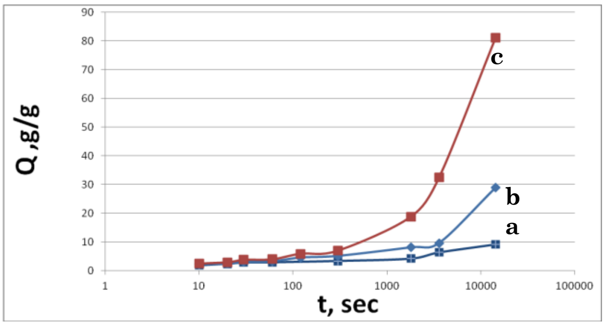

Fig. 7 – Swelling kinetics of composite based on Acrylic acid (80 wt%): a – at pH 1,86, b – at pH 7,7, c – at pH 9,57;

The studied materials are supposed to be used as carriers of various fillers, silver and magnetite particular [6,7].

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 [8-9].

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

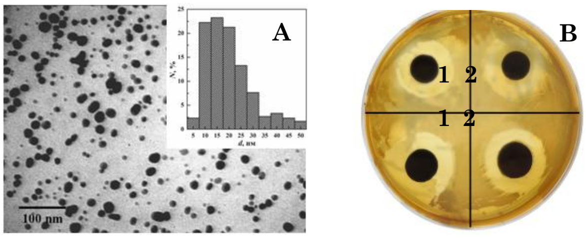

Fig. 8 – a – silver nanoparticles and their size distribution; b – test of inhibiting zones towards S. Aureus, 10^8 colonies of forming units, 1 – 0,5 wt% of silver, 2 – 1,05 wt% of silver;

4. CONCLUSIONS

Hybrid hydrogel composites were synthesized basing on PVA acetal and hydrogel copolymers of vinyl series. Silver and other nanoparticles incorporation techniques into the synthesized polymer matrices have been developed. Swelling properties in various solvents were investigated. IR comparative spectra obtained and characterized for different composites and for pure sponge. Synthesized composites based on Acrylic acid shown a good pH-sensitivity properties. High anti-bacterial action of the synthesized nanocomposites containing silver towards gram-positive and gram-negative bacteria has been demonstrated.

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