

Novel nanostructured double-network composite hydrogels based on polyacrylamide and siloxane networks

O.V. Slisenko, I.M. Bei, V.L. Budzinska

*Institute of Macromolecular Chemistry of the National Academy of Sciences of Ukraine,
48 Kharkivske sh., 02160, Kyiv, Ukraine,
E-mail: olgaslisenko@ukr.net*

Hydrogels is a kind of highly hydrophilic three-dimensional crosslinked polymeric material that attracts much attention as functional soft materials. However, in spite of wide range of their applications in medicine, biotechnology, organ engineering etc, low fracture toughness of chemically crosslinked organic polymer hydrogels substantially restricts the uses of such materials. Among many approaches to overcome this issue a basic one is an introduction of inorganic constituent into organic polymer hydrogel networks via formation of independently crosslinked double network (DN) hydrogels. Using our previous experience in this field we are able to conclude that superior functional characteristics of DN hydrogels could be achieved by formation of double polymeric networks, one of which is formed by highly crosslinked polymer, whereas another one have loosely crosslinked structure.

In this work, a novel DN nanostructured composite was developed by one-pot polymerization of organic and inorganic precursors. An organic polymer network was prepared by polymerization of acrylamide (AAm) in a presence of N,N'-methylene-(bisacrylamide) (BAAm) as a crosslinker, while inorganic siloxane network forms during catalytically-induced polycondensation process of sodium silicate (SS) precursor. A series of PAAm/SS nanoscaled hydrogels with different SS content (up to 35 wt.%) have been successfully prepared by *in situ* polymerization.

FTIR spectroscopy analysis was carried out to characterize the chemical structure of the DN nanostructured hydrogels. Complete conversion of AAm and a formation of organic PAAm network has been satisfied by disappearance of stretching vibration bands of C=C and C-H bonds of AAm with maxima at 1610 and 3080/2975 cm⁻¹, respectively. Additionally, appearance of new bands at 1682 and 1406-1410 cm⁻¹ attributed to C=O and C-N stretching vibrations of PAAm was also identified. Presence of inorganic silicate network was identified by an appearance of intensive broad band at about 1100 cm⁻¹ ascribed to the symmetric stretching vibrations of Si-O-Si bonds and a band at 789-794 cm⁻¹ attributed to the stretching vibrations of Si-O-Si bonds in three-dimensional structure [1]. Thus FTIR spectral analysis indicates a formation of DN network structure of obtained hydrogels, which consists of both organic (PAAm) and inorganic (silicate) networks.

A decreasing of the glass transition temperature (T_g) with an increasing of inorganic constituent content in comparison with pure organic network of PAAm ($T_g = 92$ °C) was observed by DSC. This fact was explained by nanostructuring of crosslinked organic and inorganic networks during the formation of DN hydrogels via interpenetrating (mixing) of organic and inorganic constituents. Non-additive decrease of heat capacity of PAAm/SS DN evidenced suppression of segmental motion of organic polymer chains in mixed phase. The thermal decomposition and weight loss profiles of PAAm and PAAm/SS DN hydrogels were estimated from TGA. The thermal stability of the samples was calculated from the initial decomposition temperature (T_{init}), the temperature of the maximum rate of mass loss (T_{max}) and the end of decomposition temperature interval (T_{end}). The PAAm/SS hybrid hydrogels degraded in a three or four-step pattern. First stage in the temperature range of 208-234 °C was attributed to the evaporation of water absorbed by hydrogel samples. The second stage since 270 to 309 °C was interpreted as a destruction of amide bonds of organic network [2]. Third stage in temperature interval of 317-410 °C belonged mainly to the degradation of the PAAm macrochains with breaking of crosslinking interchain bridges. Both 2-nd and 3-rd stages are characterized by partial weight loss with elimination of low-molecular gaseous products of degradation of PAAm constituent. Finally, a fourth degradation step in the range of 418-445 °C, which is attributed to the samples with increased SS content (25 and 35 wt.%), is related to deep degradation of organic constituent (PAAm) stabilized by highly thermostable inorganic component in mixed organic-inorganic phase. Consequently the thermograms of PAAm/SS DN nanostructured material shown enhanced thermal stability of composite samples in comparison with individual hydrogel (PAAm), due to formation of thermally stable hybrid hydrogen bonding network between amide groups of PAAm and siloxane inorganic network.

Thus a novel DN nanoscaled hydrogels consisting of organic PAAm network and inorganic siloxane network were synthesized by one-pot *in situ* polymerization. Spectral studies indicate a formation of double-network structure of obtained hydrogel composites. DSC and TGA measurements confirmed a presence of mixed organic-inorganic hybrid phase with enhanced thermal stability than that of individual PAAm homopolymer network.

This work is financially supported by complex inter-disciplinary scientific program of NAS of Ukraine on the problems of constant development, rational nature management and environmental protection (project N. 32).

1. Li P., Kim N.H, Hui D., Rhee K.Y., Lee J.H. Improved mechanical and swelling behavior of the composite hydrogels prepared by ionic monomer and acid-activated Laponite // *Applied Clay Science*. – 2009. – 46. – P. 414–417.
2. Biswal D.R., Singh R.P. Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer // *Carbohydrate Polymers* – 2004. – 57. – P. 379–387.