

Synthesis and Characterization of Polyacrylamide / Siloxane Double Network Hydrogels

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(Received 31 May 2015; published online 26 August 2015)

A novel double-network (DN) hydrogels consisting of organic polyacrylamide (PAAm) network and inorganic siloxane network were synthesized by one-pot *in situ* polymerization. Spectral studies indicate a formation of DN structure of composite hydrogels obtained. Detailed study of the composites showed well-defined structuring of hybrid hydrogels at molecular and nanolevel as well as intra- and intercomponent interactions via H-bonding. Nanostructurization possesses a great impact on final properties of the composite hydrogels. Prepared materials are characterized by improved thermal stability and hydrophilicity. Swelling degree of hybrid composite hydrogels depends on components ratio and reaches 2700 %.

Keywords: organic-inorganic hybrid hydrogels, swelling of hydrogels, sodium silicate, polyacrylamide, hydrophilic.

PACS numbers: 82.35.Np, 81.16.Be

1. INTRODUCTION

Producing new nanocomposite hydrogels with high mechanical and sorption characteristics attracts much scientific interest last years. Several methods to create organic-inorganic composite hydrogels (OIC) such as introduction of polymer particles [1, 2], nanoclays [3, 4] and carbon nanotubes [5] into the polymer or monomer with subsequent cross-linking and formation of (semi)-interpenetrating (sIPN/IPN) polymer networks [6, 7], or formation of independently cross-linked double network hydrogels [8] are used. So, wide range of different types of OIC with various phase structures from the formation of structures polymer matrix – nano-/micro-sized till OIC with double phase continuity inclusions were obtained. Stabilization of hydrogel structure is occurred due to formation of H-bonds and interpenetrating of macromolecular chains in sIPN/IPN. Effect of polymer chains mixing is supplemented with physical interactions of polar groups and gives new possibilities to create composite materials with improved properties.

In order to improve strength, hardness, thermal stability and other properties of organic hydrogels the inorganic components should be introduced. The process of introduction of inorganic component into organic hydrogels can be conditionally divided into two groups: 1) cross-linking of water-soluble polymers or monomers in aqueous clay dispersion [3, 9]; 2) introduction of precursors of inorganic components in solutions of monomers or polymers followed by consequent or simultaneous cross-linking of organic or inorganic phases [8, 10].

It is possible to regulate properties of OIC by changing organic / inorganic constituents ratio, thus an inorganic dispersible component performs reinforcing function, provides improved physical-chemical characteristics and crack resistance.

Silica reinforced double-network structure hydrogels is one of the most popular approach of last years.

The introduction of silica particles into polymer phase leads to the polymer-silica interaction in the hydrogels, besides covalent, non-covalent and ionic bonds. As results, mechanical strength of the hydrogels (modulus and fracture stress) of silica-filled systems increases up to 3 times in comparison with virgin hydrogels as well as elasticity of these materials keeps at appropriate level [11].

In spite of intensive researches of hydrogel materials the only insignificant part of works is dedicated to the study of influence of structural features and intercomponent interactions on final properties of OIC hydrogels. In this paper a novel DN organic-inorganic hydrogel with high absorption ability based on PAAm and silica, obtained by *in situ* condensation of SiO₂ from sodium silicate (SS) and studied the effect of organic/inorganic ratio on a structure, thermal properties and hydrophilicity of the hydrogels obtained.

2. EXPERIMENTAL

2.1 Materials

A novel DN nanostructurized composite hydrogels were synthesized by simultaneous cross-linking technology, which includes a combination of free radical polymerization of acrylamide (AAm) in a presence of N,N'-methylene-bis(acrylamide) (BAAm) cross-linker and catalytically-induced polycondensation process of orthosilicic acid in aqueous solution. Predetermined amounts of AAm, BAAm, an radical initiator (ammonium persulfate) and a promoter (N,N,N',N'-tetramethylethylenediamine) were dissolved in distilled water. As-prepared aqueous solution of SS (20 wt.%, molar ratio SiO₂/Na₂O = 2.85±0.05) was added dropwisely into monomers solution under stirring. Simultaneous polymerization of AAm/BAAm into crosslinked PAAm and condensation of orthosilicic acid (NH₄⁺ ions act as initiators of polycondensation process) into highly dispersed SiO₂ were carried out at 70-80 °C for 5 hours.

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Obtained samples were purified by thoroughly washing by distilled water for removing of unreacted monomers. Hybrid composite hydrogels with different SiO₂ content (from 5 to 35 % by weight) were successfully prepared.

2.2 Methods

FTIR spectra of composites were recorded on a Bruker Tensor 27 DTGS spectrometer at wavenumber range of 4000 – 600 cm⁻¹ with a resolution of 2 cm⁻¹.

Calorimetric studies (DSC) was conducted using DSC Q2000 (TA Instruments) calorimeter under nitrogen flux with a programmed heating rate of 20°C min⁻¹. The second heating scan (within temperature interval of 25 – 200°C) was taken for analysis. The temperature dependence of a heat capacity C_p was determined and the midpoint of the endothermic jump of the function C_p=f(T) was taken as a glass transition temperature (T_g).

Thermal stability of the samples was studied by thermogravimetric analysis (TGA) using the TGA Q-500 (TA Instruments) equipment. TG traces were registered in the temperature range from 25 to 800°C at a heating rate of 20°C min⁻¹ in nitrogen at continuous evacuating of volatile products of degradation.

A swelling behaviour of composite hydrogels in distilled water media was monitored by gravimetry at 20 °C. The sample was immersed into large amount of distilled water. The hydrogel was separated from water at regular time intervals to measure the changing a weight of the sample. The measurements were continued until equilibrium was reached. The swelling degree (water uptake) (*q*) was calculated using equation:

$$q = (m_w - m_d) / m_d \cdot 100\%,$$

where *m_w* – weight of swelled sample; *m_d* – weight of dried sample.

3. RESULTS AND DISCUSSION

The formation of both networks during polymerization of AAm and polycondensation of silicate constituent was confirmed by FTIR (Fig. 1). FTIR spectra of PAAm/SiO₂ samples are characterized by the presence of specific absorption bands, which were assigned to the acrylamide fragments of polymer macrochains: 3420-3426 cm⁻¹ (ν_{as}NH), 3190-3194 cm⁻¹ (ν_sNH), 2923-2928 cm⁻¹ (νCH), 1665-1667 cm⁻¹ (ν_sC=O), 1613-1619 cm⁻¹ (δNH) and 1406-1410 cm⁻¹ (νCN) [12]. Absence in the spectra of the composites of absorption bands at 3080 and 2975 cm⁻¹ (stretching vibrations of C-H bonds of unsaturated =CH₂ and =CH-groups of acrylic monomer) is observed due to polymerization of AAm into PAAm while the hybrids form.

Inorganic component in hybrid hydrogels (SiO₂) is also characterized by few typical absorbance bands. Superposition of asymmetric and symmetric stretching vibrations of Si-O-Si bonds results in a broad absorption band with a maximum at 1100 cm⁻¹. The band at 789-794 cm⁻¹ is assigned to symmetric stretching vibrations of O-Si-O bond in three-dimensional siloxane network structure [13]. A presence of adsorbed water in the structure of composites, that is very typical for hydrogel materials, is identified by characteristic bands at 3300 and 1640 cm⁻¹.

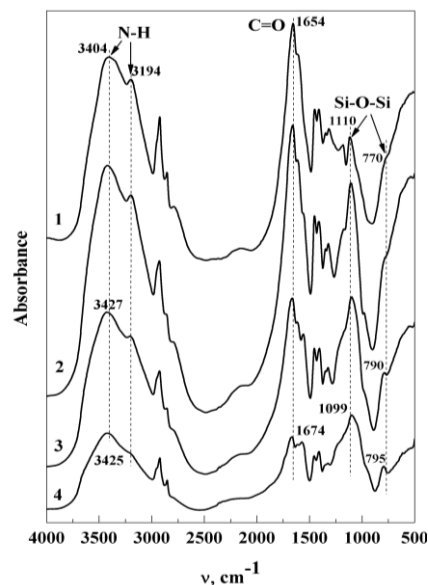


Fig. 1 – FTIR spectra of hybrid PAAm/SiO₂ hydrogels at different SiO₂ content (wt.%): 0 (1), 15 (2), 25 (3) and 35 (4).

Thus proposed synthetic pathway is allowed to create both organic and inorganic networks and to obtain hybrid PAAm/SiO₂ composites with dual network structure.

Interaction between organic and inorganic polymer networks that has a great impact on characteristics of such composites was also studied by FTIR. Fig. 1 shows shifts of absorption bands ν_{as}NH by 25 cm⁻¹ and ν_sC=O by 9-11 cm⁻¹ to high-frequency spectral region with increasing SiO₂ content up to 35 wt.%. It takes place due to weakening of intramolecular hydrogen bonds of amide fragments of PAAm networks as a result of shearing organic polymer macrochains by inorganic siloxane network formed from silicate precursor and appearing inter-component interaction between the constituents of different nature (adsorbed water molecules have an effect on inter-/intracomponent interactions of the composites).

Intermolecular interactions between organic and inorganic phase should affect thermophysical properties of hybrid composites. Calorimetric studies of the samples were conducted to evaluate changes in relaxation behaviour of polymer constituent and the results were summarized in Table 1. Decreasing glass transition temperature (T_g) of PAAm macrochains in hybrid composites with increasing inorganic component content in comparison with individual PAAm (T_g = 92 °C) was clearly identified. This fact is directly evidenced of a formation of double network structure of composite hydrogel while polymerization (polycondensation) of organic and inorganic spatial networks carried out.

Table 1 – Thermophysical properties of PAAm/SiO₂ composites

Sample	T _g , °C	T _{g(onset)} , °C	T _{g(end)} , °C	ΔC _p , J/g·°C	ΔC _{p-add} , J/g·°C
PAAm	92	80	107	0.338	0.338
PAAm/SiO ₂ 85/15	79	70	94	0.330	0.287
PAAm/SiO ₂ 75/25	81	70	98	0.280	0.254
PAAm/SiO ₂ 65/35	58	54	60	0.097	0.220

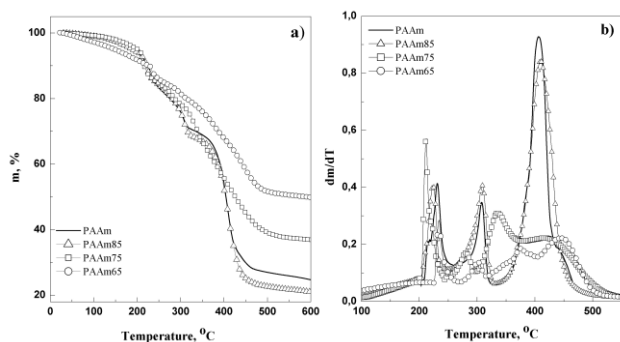


Fig. 2 – TG (a) and DTG (b) curves of hybrid PAAm/SiO₂ hydrogels

Thermal decomposition and weight loss profiles of PAAm/SiO₂ hybrid hydrogels were estimated from TGA thermograms as a function of temperature, as it shown in Fig. 2.

It was found that thermal destruction of PAAm/SiO₂ composites is highly depends on inorganic phase content and occurs in 3-4 steps. The 1st step depicts the loss of moisture adsorbed by the samples [14]. The second stage with maximum at ($T_{d(max)}$) at about 280-308 °C concerns to a degradation of side amide groups (bonds) in organic network [15]. At temperature interval of 317-410 °C the 3rd step related to decomposition of hydrocarbon chains of PAAm and intermolecular cross-links is observed. The 4th stage with $T_{d(max)}$ at 422 and 445 °C, was identified for samples PAAm/SiO₂ with SiO₂ content of 25 and 35 wt.%, respectively.

From the analysis of swelling behavior of the hydrogels it was established that at the beginning of sorption process the rate of sorption is rather high and is in accordance with Fickian law. PAAm/SiO₂ nanostructured hydrogels could be characterized by two-stage swelling model: (1) a rapid increase of the solvent content in the composite that takes place due to PAAm saturation and then after some quasi-equilibrium (2) the solvent concentration increased much slowly. The swelling degree of PAAm/SiO₂ 75/25 composite reaches 2700 %.

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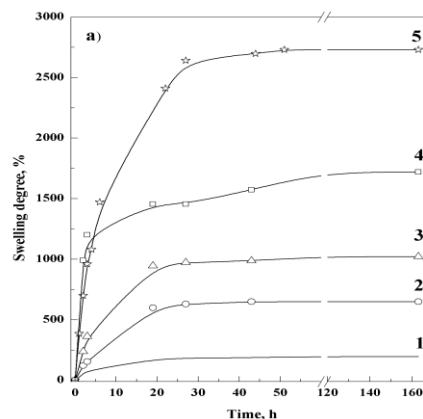


Fig. 3 – Swelling profile of hybrid hydrogels as a function of time at different SiO₂ content (wt.%): 0 (1), 5 (2), 15 (3), 25 (5) and 35 (4).

4. CONCLUSIONS

The composite lyophilic organic-inorganic PAAm/SiO₂ hydrogels with double-network structure were prepared by *in situ* polymerization of AAm and SiO₂. FTIR spectra and DSC analysis indicated the formation of network structure and confirmed decreasing of H-bonds quantity in PAAm with SiO₂ content increasing due to formation of mixed PAAm/SiO₂ phase. The experimental results of structurizing of hybrid hydrogels on molecular and nanolevel and inter-component interaction by means of H-bonds indicate improvements in the thermal stability and swelling ratio.

ACKNOWLEDGEMENTS

The authors are grateful to the authority of the Center of Collective Use of Scientific Equipment of the National Academy of Science of Ukraine (NASU) "Thermophysical investigations and analysis" in Institute of Macromolecular Compounds of NASU for providing DSC and TGA.

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