



Novel highly hydrophilic organic/inorganic composites based on polyacrylamide and silica: synthesis strategy, structure and swelling behaviour

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Abstract

A series of novel hydrophilic organic-inorganic composites (OIC) with enhanced sorption properties were synthesized by one-pot synthesis technique - in situ radical polymerization of acrylamide (AM) and hydrolytic polycondensation of sodium silicate in aqueous solution. Formation of mixed organic-inorganic polyacrylamide (PAM)/SiO₂ phase has been detected by FTIR spectroscopy (appropriate changes in H-bonds network structure of PAM) and DSC analysis (dramatic decreasing glass temperature of PAM). Additive decreasing of mass loss of OIC with increasing of SiO₂ content is explained by the increasing of PAM-content in mixed PAM/SiO₂ phase on the interface of organic and inorganic phases. The formation of SiO₂ aggregates with different dispersity, which, in their turn, form submicron structures in composites with SiO₂ content more than 15 wt.% was observed from SEM data. Structurization of OIC resulted in the enhanced sorption characteristics (swelling capacity of the OIC reaches 2730%). Sorption kinetic curves obtained both in isothermic and isochoric regimes demonstrate that the swelling process of OIC is limited by relaxation of PAM chains and can be described by sorption mechanism of Type II.

Keywords Composite · Hydrogel · Swelling pressure kinetics · Structure-property relations

Introduction

Development of organic-inorganic composite hybrid hydrogels with reinforced mechanical and enhanced sorption properties have attracted great interest in the last decade [1, 2]. New types of hydrogel have been developed using different strategies including nanocomposites (NC) gels with polymer-clay networks [3, 4], introduction of nanostructured minerals or carbon nanotubes into the polymer or monomer [5] and subsequent polymerization with formation of (semi-) interpenetrating polymer networks (sIPN/IPN) [6, 7], or so called «double-network» structures [8]. So, wide range of different types of OIC with various phase structures from the formation of polymer matrix – nano-/micro-sized structures OIC with double phase continuous inclusions were obtained. Stabilization of the 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 ways to create composite materials with improved properties.

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

Since an inorganic dispersible component performs reinforcing function, providing improved physical-chemical characteristics and crack resistance, it is possible to regulate properties of OIC by changing organic/inorganic constituent's ratio. Silica reinforced polymer composite hydrogels is one of the most popular approach in last years. The introduction of silica particles into

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polymer phase leads to the polymer-silica interaction in the hydrogels, in addition to the covalent, non-covalent and ionic bonds. As a result, mechanical strength of the hydrogels (modulus and fracture stress) of the silica-filled systems increases up to 3 times in comparison with the virgin hydrogels while the elasticity of these materials remains at the appropriate level [2–8].

A new type of nanocomposite gel composed of a ternary poly(N-isopropylacrylamide)-clay-silica system (NC-Si), was synthesized [11] by incorporating a small amount of silica (0.2–2.5 wt% relative to the gel weight) through the sol-gel reaction of tetraethyl orthosilicate (TEOS) in the polymer-clay network. These NC-Si gels exhibited anomalous increases in mechanical stiffness and tensile strength (~1700 kPa), very high tensile moduli (~3500 kPa).

A dual nanocomposite hydrogel with inorganic hybrid crosslinking poly(acrylamide-co-methacrylic acid)/Laponite/SiO₂ was fabricated [12] through simultaneous sol-gel technique and free radical polymerization. Due to the multi-strengthening mechanism, the hydrogel was super tough and strong with a compressive stress of 32 MPa without rupture even at 100% strain, while it exhibited excellent fatigue resistant properties. The presence of covalent bonds between SiO₂ and Laponite was proved, as well as between polymers and SiO₂, which strengthened the compatibility of inorganic fillers with polymer matrixes.

Authors [13] studied the thermo-responsive hydrogels based on polyvinyl chloride (PVC) with enhanced mechanical properties by the incorporation of inorganic cross-linked silica phases in an organic aqueous PVC phase. The strength improvement was based on the existence of physical entanglements and interactions (hydrogen bonds) between the organic PVC macromolecules and the inorganic silica particles. Equilibrium swelling degrees of the PVC hybrid hydrogels varied from 560 to 3000%. Concerning the thermo-responsive properties of the hybrid materials, no remarkable influence of silica on the cloud point temperature of PVC was observed. However, it was found that the presence of silica decreases considerably the thermo-sensitive response rate.

For the development of sealing products based on highly absorbing polymers, information about the swelling pressure is of essential significance. Detailed analyses, regarding mechanisms and inter-relations between polymer structure and the amount of inorganic constituent sealing volume and sealing performance, are lacking. Nowadays, several different methods can be used for the determination of the swelling pressure of hydrogels, such as the analysis of the swelling pressure at a given pressure [14], membrane osmometric determination of the swelling pressure [15, 16], analysis of the swelling pressure at a given final volume of swelling [17].

In spite of intensive investigations 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. The application of organic

hydrogels is limited by restricted molecular motions of polymer chains caused by cross-linking with a number of organic cross-linkers. Furthermore, the most serious limitations of organic gels are due to their weak and brittle nature as well as insufficient swelling. In order to overcome some limitations of polyacrylamide (PAM) gels, we succeeded in synthesizing a new type of OIC hydrogel based on aqua solution of sodium silicate. Prepared PAM/SiO₂ hydrogels showed remarkable improvements in swelling properties, thermal stability, also in strengthening of the molecular structure of the composite as a result of reinforcing the organic network by inorganic one. This was found by carrying out the swelling pressure measurement. Inorganic component acts as multifunctional cross-linking agents through noncovalent interactions instead of using organic cross-linkers.

In this paper a novel network organic-inorganic hydrophilic composites with high absorption ability based on PAM and silica, obtained by in situ condensation of SiO₂ from water solution of sodium silicate was studied as well as the effect of organic/inorganic ratio on a structure, thermal properties and hydrophilicity of the hydrogels obtained. The choice of the inorganic component was due to the main features of silicates and first of all their availability and the high temperature stability. Sodium silicate water solution does not contain any solvents and even at high temperatures it does not produce harmful vapours or gases. In addition, obtaining SiO₂ from the liquid phase ensures perfect homogeneity of the system in contrast to the case of introducing solid particles of SiO₂ which can aggregate. Sorption kinetics and the swelling pressure in isothermic and isochoric conditions of polymer hydrogels were studied in details.

Materials

Acrylamide (AM) and the initiator - ammonium persulfate (APS) were bought from Merck (Darmstadt, Germany) and used without further purification. N,N'-methylenebis(acrylamide) (MBA) cross-linker and promoter (N,N,N',N'-tetramethylethylenediamine, TEMED), aqueous solution of sodium silicate (water glass) were supplied by Aldrich Chemicals (Milwaukee, US) and used as received. Sodium silicate water solution has a modulus SiO₂/Na₂O = 2.85 ± 0.05. Deionized water (DW) was utilized in all the experiments.

Sample preparation

Synthesis of a novel organic-inorganic composite hydrogels with IPN structure were fulfilled by simultaneous cross-linking processing, which includes a combination of free radical polymerization of AM in a presence of MBA cross-linker and catalytically-induced polycondensation process of sodium

silicate in aqueous solution. Predetermined amounts of AM, MBA, radical initiator (APS) and TEMED were dissolved in DW. As-prepared aqueous solution of sodium silicate (52 wt.%) was added dropwise into monomer solution under stirring. Simultaneous polymerization of AM/MBA into crosslinked PAM and condensation of sodium silicate (NH_4^+ ions act as initiators of polycondensation process [18]) into highly dispersed SiO_2 were carried out at 70–80 °C for 5 h. Obtained samples were purified by washing with distilled water for removing of unreacted monomers. Hybrid composite hydrogels with different SiO_2 content (from 5 to 35% by weight) were successfully prepared.

Methods

Fourier-transform infrared spectroscopy (FTIR)

Dried and pounded hydrogels powder was pressed with KBr and FTIR spectra of the composite hydrogels were recorded with a Bruker Tensor 27 DTGS spectrometer at wavenumber range of 4000–600 cm^{-1} with a resolution of 2 cm^{-1} . The spectra were normalized by height before spectra subtraction was performed.

Differential scanning calorimetry (DSC)

Calorimetric studies was conducted using DSC Q2000 (TA Instruments) calorimeter in nitrogen atmosphere with heating rate of 20 °C min^{-1} . The second heating scan (within temperature interval of 25–200 °C) was taken for analysis to define glass transition temperature (T_g) and heat capacity (C_p).

Thermogravimetric analysis (TGA)

Thermal stability of the samples was studied by 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 flux at continuous evacuating of volatile products of degradation.

Scanning electronic microscopy (SEM)

Morphology of the dehydrated samples was studied by SEM using the JEOL JSM 6060 LA instrument at an accelerating voltage of 30 kV.

Swelling properties

The swelling ability of gels in a free state in isothermic regime 18 ± 1 °C was studied by immersion of dried sample in water. The sample was placed in the swelling solution (water) and the weight of the swollen sample was measured along the sample exposition periodically taking out and weighting the

sample (time of measuring was <1 min). Before weighting the excessive surface water was removed by gently touching of a dry filter paper. The degree of swelling (w_t) for each sample at time t was calculated using equation:

$$w_t = \frac{m_t - m_0}{m_0}, \quad (1)$$

where m_t and m_0 are the sample weight at any given time, and in the initial dry state, respectively.

Swelling pressure measurements

The swelling pressure kinetics of the PAM/ SiO_2 gels was determined by a homemade swelling pressure meter. The device consists of a calibrated transducer (which convert pressure, produced by a sample, into an electrical signal), and a sample chamber that contains the gel. The sample was covered by fixed permeable membrane (permeable to water but impermeable to a sample material) which was jointed with transducer recording a pressure of gel under membrane without change of the gel volume. Thus, measurements of swelling pressure were carried out in isochoric conditions at 18 ± 1 °C.

Results and discussion

Chemical structure characterization

The formation of both networks during the polymerization of AM and polycondensation of silicate constituent was confirmed by FTIR (Fig. 1). Inorganic network formation is based on hydrolysis of Na^+ -form of polysilicic acid with its subsequent condensation at presence of NH_4^+ .

Absence in the spectra of the absorption bands at 3080 and 2975 cm^{-1} (stretching vibrations of C-H bonds of unsaturated = CH_2 and = CH -groups of acrylic monomer) is observed due to polymerization of AM into PAM. A presence of absorbed water in the structure of composites is identified by characteristic band at 3300 cm^{-1} .

FTIR spectra of PAM/ SiO_2 samples showed the presence of specific absorption bands, which were assigned to the acrylamide fragments of polymer macrochains: 3420–3426 cm^{-1} ($\nu_{\text{as}}\text{NH}$), 3190–3194 cm^{-1} ($\nu_{\text{s}}\text{NH}$), 2923–2928 cm^{-1} (νCH), 1665–1667 cm^{-1} ($\nu_{\text{s}}\text{C=O}$), 1613–1619 cm^{-1} (δNH) and 1406–1410 cm^{-1} (νCN) [19].

Inorganic component (SiO_2) in OIC hydrogels is also characterized by 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 peak at 789–794 cm^{-1} is assigned to the symmetric stretching vibrations of O-Si-O bond in the three-dimensional siloxane network structure [18].

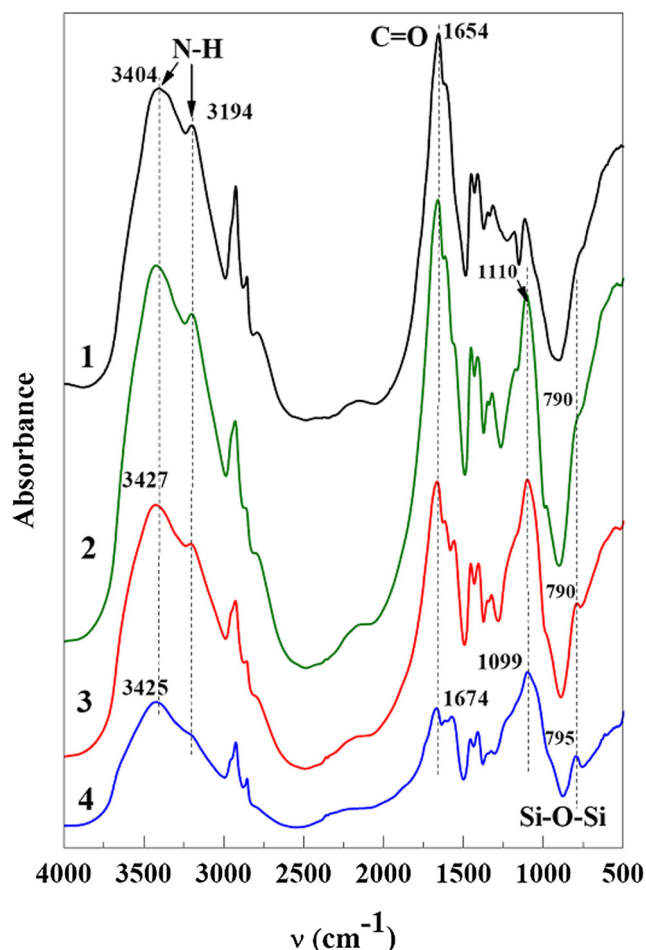


Fig. 1 FTIR spectra of PAM/SiO₂ OIC hydrogels at different SiO₂ content (wt.%): 0 (1), 15 (2), 25 (3) and 35 (4)

Interaction (via H-bonds) between organic and inorganic polymer networks that has a great impact on characteristics of such composites was also revealed by FTIR. Figure 1 shows shifts of $\nu_{\text{as}}\text{NH}$ absorption bands by 25 cm^{-1} and $\nu_{\text{s}}\text{C=O}$ by 9–11 cm^{-1} to high-frequency spectral region. Si-O stretching vibrations (1090–1104 cm^{-1}), which are sensitive to the inorganic component distribution, show shifts toward lower wavenumbers at increasing of SiO₂ content up to 35 wt.%. This phenomenon takes place due to weakening of the intramolecular hydrogen bonds of amide fragments of PAM networks as a result of detachment of the organic polymer macrochains by inorganic siloxane network. These changes are explained by appearing of intercomponent interactions between the constituents of different nature (absorbed water molecules affect on inter-/intracomponent interactions of the composites) [20].

Morphology of hybrid PAM/SiO₂ composites

Analysis of SEM photos of PAM/SiO₂ shows that the presence of inorganic constituent leads to the appearance of heterogeneous structure. The formation of SiO₂ aggregates with

different dispersity, which, in their turn, form submicron structures in composites with SiO₂ content more than 15 wt.% was observed from SEM data (Fig. 2).

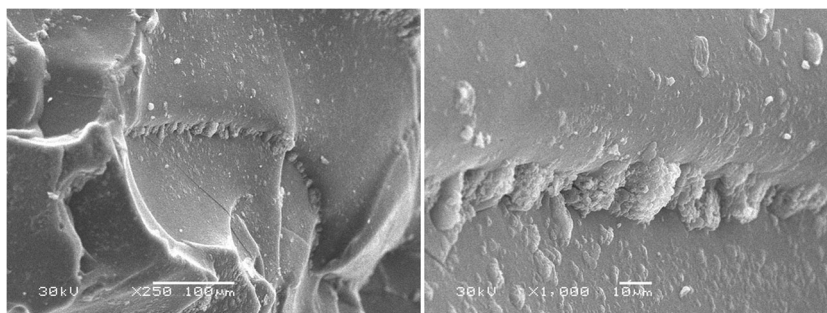
Thermal stability of highly hydrophilic PAM/SiO₂ composites

The thermal decomposition (weight loss profiles) of PAM/SiO₂ hybrid hydrogels were estimated via thermogravimetry (TG) and differential thermogravimetry (DTG) as a function of temperature, as shown in Fig. 3. It was revealed that thermal destruction of nanostructured PAM/SiO₂ composites occurs in 3 separated regions (200–250, 250–350 and 350–500 °C) according to DTG where 3–4 peaks loss DTG can be allocated and which depend on the content of the inorganic constituent. The first step depicts the loss of moisture absorbed by samples. Also the decomposition peak at 211–234 °C relates to the destruction of amide bonds in organic network [21]. The second step of degradation is appeared at 278–308 °C and can be attributed to the degradation of PAM hydrocarbon chains and intermolecular crosslinking. For the composites with SiO₂ content 25 and 35 wt.%, respectively. The loss weight maximum $T_{\text{d(max)}}$ at 335 and 375 °C, respectively, can be explained by decomposition of PAM-constituent in mixed PAM/SiO₂ – phase. Deep decomposition of PAM-constituent at highest temperature is identified for PAM and PAM/SiO₂ = 85/15 samples by $T_{\text{d(max)}}$ at 406 and 410 °C, respectively. Decomposition of PAM macrochains in hydrophilic composites with increased content of inorganic component is observed at high temperatures: at 422 °C (PAM/SiO₂ = 75/25 wt.%) and 444 °C (PAM/SiO₂ = 65/35 wt.%) in comparison to individual PAM ($T_{\text{d(max)}} = 406$ °C). The higher temperature of decomposition can be explained by the process of organic constituent stabilization (insulation) by thermostable inorganic component in mixed organic-inorganic phase.

It is necessary to note additive decreasing of mass loss with increasing of SiO₂ content for 1st and 2nd stages of destruction. At the same time it was observed decreasing of experimental Δm_i in comparison with additive values at the decomposition of PAM-macrochains and intermolecular cross-links. This fact can be explained by the increasing of PAM-content in mixed PAM/SiO₂-phase on the interface of organic and inorganic phases. Consequently, the thermograms of PAM/SiO₂ composites have shown enhanced thermal stability of composite samples in comparison with individual PAM hydrogel, due to formation of thermally stable mixed organic-inorganic phase via hydrogen bonds between amide groups of PAM and siloxane inorganic network. The corresponding heat-resistance index (T_{HRI}) of the PAM/SiO₂ composites was calculated by Eq. (2) [22, 23]:

$$T_{\text{HRI}} = 0.49 \cdot (T_5 + 0.6 \cdot (T_{30} - T_5)) \quad (2)$$

Fig. 2 Typical SEM micrographs of PAM/SiO₂ = 75/25 composite at different scale



where T_5 and T_{30} are the corresponding decomposition temperatures of 5% and 30% weight loss, respectively, and shown in Table 1. It was revealed that the thermal stabilities of the PAM/SiO₂ composites were obviously enhanced, that can be explained by better interfacial compatibility between PAM and SiO₂.

The essential decreasing of glass temperature (T_g) of PAM-macrochains in hydrophilic composites with increasing of inorganic component content in comparison with individual PAM ($T_g = 92$ °C) can be seen from Table 1.

This fact evidences about disorganization of H-bonds network of PAM during polymerization (polycondensation) of organic and inorganic spatial networks and formation of interpenetrating networks structure of hydrogel. ΔC_p and ΔC_{p-add} columns of Table 1 show the experimental and calculated (by additive rule) values of heat capacity, respectively. Non-additive decreasing of heat capacity of PAM/SiO₂ composites indicates an increasing of segmental mobility of PAM-macrochains.

Swelling and swelling pressure of initial PAM and PAM/SiO₂ hydrophilic composites

The kinetic dependences of swelling in the free state for PAM/SiO₂ hydrophilic composites are shown in Fig. 4a. The data illustrate that the introduction of the inorganic component into

the PAM network causes significant increasing of the sorption capacity w_t (g of H₂O / g of composite) of the composites. This fact can be explained by following factors: (1) the formation of organic and inorganic networks, which leads to the appearance of a significant fraction of the mixed organic-inorganic phase and (2) their high hydrophilicity.

The sorption process is associated with the formation of bridging groups (H₂O)_m between the fragments in the individual organic and inorganic phases and in the mixed PAM/SiO₂ phase. Thus, the high hydrophilicity of hydrogel's constituents of organic and inorganic networks at the molecular and nano-scale levels provide the destruction of intra- and intermolecular N-H...O=C bonds and formation of H-bonds with H₂O molecules [24]. This results in a high degree of swelling of hydrogels, for example 2730% (PAM/SiO₂ = 75/25) compared to the neat PAM of 186%.

In general, the process of sorbate diffusion into the polymer is determined by two factors: the migration rate of the sorbate molecules through the polymer network and the relaxation rate of the macrochains of a matrix when they are rearranged during the sorption process. The kinetics of sorbate diffusion into a polymer can be classified by two types of diffusion [25, 26]. Type I diffusion (Fickian diffusion) exists in the case of fast relaxation of polymer chains when the sorption process is limited by the rate of sorbate diffusion into the polymer (diffusion-controlled kinetics). Type II diffusion (non-Fickian) is

Fig. 3 Weight loss TG curves (a) and derivative DTG curves (b) of PAM/SiO₂ hybrid hydrophilic composites

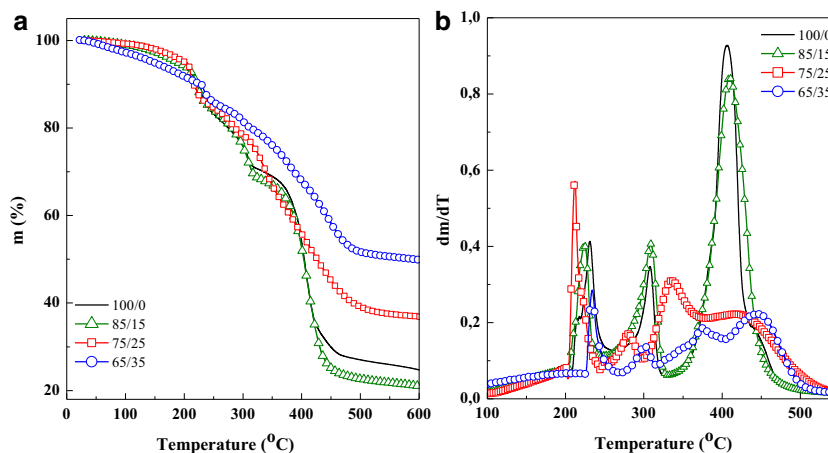


Table 1 Thermal properties of PAM/SiO₂ composites

Sample	$T_g, ^\circ\text{C}$	$\Delta C_p, \text{J/g}\cdot\text{K}$	$\Delta C_{p\text{-add}}, \text{J/g}\cdot\text{K}$	Weight loss temperature, $^\circ\text{C}$		$T_{\text{HRb}}, ^\circ\text{C}$
				T_5	T_{30}	
PAM	92	0.338	0.338	184	335	134.6
PAM/SiO ₂ 85/15	79	0.330	0.287	189	316	130.0
PAM/SiO ₂ 75/25	81	0.280	0.254	201	339	139.1
PAM/SiO ₂ 65/35	58	0.097	0.220	148	388	143.1

characterized by a diffusion rate exceeding the relaxation rate, and the sorption process is limited by the relaxation rate of polymer chains (relaxation-controlled kinetics). Generally, the amount of sorbate w_t in time t (K is a constant) can be expressed as [26]:

$$w_t = K \cdot t^n \quad (3)$$

In case of Fickian diffusion $n=0.5$ and w_t will be a linear function of time $\sqrt{t}$ for the initial sorption stage. For the diffusion of Type II value $n=1$ and w_t is a linear function of the sorption time t . For this type of diffusion, a relaxation model was proposed in which the rearrangement of polymer chains is considered as a response to the sorption and the diffusion process rate is determined by the relaxation time τ_R [27, 28]. The third case, non-Fickian anomalous diffusion, is between types I and II, with $0.5 < n < 1$ and the w_t values vary similarly to s-shape from one type to another [26, 29, 30].

Authors [30–33] proposed to consider the sorption process as a sum of diffusion types I and II:

$$w(t) = w_{mF}[1 - \exp(-k_F t)] + w_{mR}[1 - \exp(-k_R t)] \quad (4)$$

where: $w(t)$ is the volume of absorbed water; w_{mF} and w_{mR} – are the equilibrium sorption values for the Fickian and relaxation diffusion case and $w_{mF} + w_{mR} = 1$; k_F and k_R are the rate

constants for the first and the second types of diffusion. The rate constant of Fickian diffusion equals [31]:

$$k_F = \frac{4\pi^2 D_F}{l^2} \quad (5)$$

where: D_F is the sorbate diffusion coefficient; l is the thickness of the sample. The rate constant of the sorption process for the relaxation case is determined by the relaxation time [33, 34]:

$$k_R = \frac{1}{\tau_R} \quad (6)$$

In double logarithmic coordinates, Eq. (3) takes the form:

$$\log w_t = \log K + n \log t \quad (7)$$

n is determined by the slope of the linear segment of the initial stage of sorption. In Fig. 4b the experimental values of normalized sorption w_t/w_m are presented in coordinates of Eq. (7) and corresponds well to $n=1$. Thus, in our case, the swelling of the hydrogel proceeds through diffusion of type II. Then Eq. (4) for PAM/SiO₂ takes the form:

$$w_t = w_m[1 - \exp(-k_R t)] \quad (8)$$

Figure 4b demonstrates the calculated values of w_t/w_m in accordance with Eq. (7), which are in good agreement with experimental values (solid line). Calculation for $n=0.5$ gives

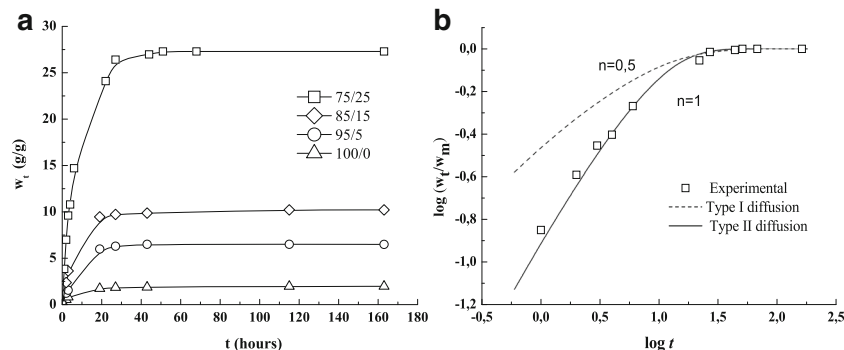


Fig. 4 **a** - sorption isotherms of PAM/SiO₂ composites with a component ratio: 100/0, 95/5, 85/15 and 75/25 wt.% (lines are related to the dependencies calculated according to Eq. (8), points are experimental values (relative amount of sorbed water was calculated from Eq. (1)); **b** - the

kinetic curves of sorption for PAM/SiO₂ = 75/25 sample in coordinates of Eq. (7). Experimental values are marked by points, solid line shows values calculated in accordance with Eq. (8) for Type II diffusion ($n=1$), dotted line shows values calculated for Type I (Fickian) diffusion

Table 2 Kinetic parameters of sorption in the free state at isothermic (w_m , k_R) and at isochoric (P_m , k_{Rp}) conditions

Sample	$w_m \cdot 100$, %	$k_R \cdot 10^3$, min ⁻¹	P_m , MPa	$k_{Rp} \cdot 10^3$, min ⁻¹
PAM/SiO ₂ = 100/0	186	2.67	1.38	24.0
PAM/SiO ₂ = 95/5	655	2.00	1.31	7.8
PAM/SiO ₂ = 85/15	1020	2.00	1.46	8.0
PAM/SiO ₂ = 75/25	2730	1.83	1.49	12.0

result that is faraway of experimental points (dotted line). Data calculated from Eq. (8) for all studied composites are presented in Fig. 4a and Table 2.

It is obvious from these data that the equilibrium (maximum) of sorption value w_m rapidly increases with increasing of SiO₂ content. At the same time, a decrease in the values of the rate constant k_R indicates an increase in the relaxation time τ_R , which agrees with the DSC data (see Table 1), and is evidence of formation of two networks in the structure of hydrogel. At increasing of the inorganic phase content the composite becomes stiffer this leads to the rising of the relaxation time of the chains forming free volume (decreasing of T_g) during the swelling process. This approach can be adapted for description the swelling pressure during sorption in polymer systems under isochoric conditions (at constant volume of the sample during sorption).

The appearance of the swelling pressure can be explained by the penetration of sorbate molecules into the surface layer, which is accompanied by the deviation of a single element of the macrochain of the polymer. In turn, the movement of monomeric units of polymer causes the appearance of local forces. As a result, a field of mechanical forces induced by diffusion fluxes is raised. Thus, the pressure on the polymer chains, which are surrounded by sorbate molecules, develops during the swelling process.

The process of sorption of the sorbate in the polymer continues until the elastic tension of the swollen gel is balanced by the swelling pressure, after which the gel remains in the

swollen state. In accordance with the foregoing, the capacity of the polymer gel is determined by two parameters - the osmotic pressure of swelling and the elastic modulus of the polymer [34, 35]. The swelling pressure depends on the energy of interaction between polymer molecules and sorbate, its concentration in the swollen system and sorption conditions.

The representation of the kinetic dependences on the swelling pressure in the coordinates of Eq. (7) showed that these dependences are not described by the Fickian model. Therefore, a relaxation-type diffusion model was used to analyse the results obtained. In this case, the change in the swelling pressure during sorption can be described by the equation:

$$P_t = P_m [1 - \exp(-k_{Rp}t)] \quad (9)$$

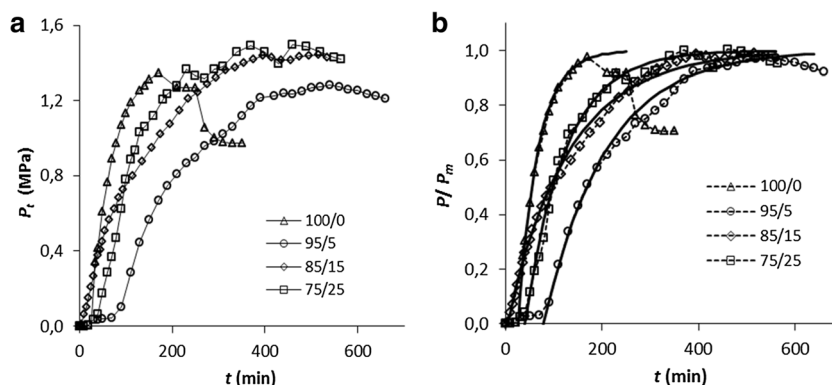
where P_m - is the prefactor determining the equilibrium swelling pressure, k_{Rp} - is the rate constant of relaxation under constant volume conditions, k_{Rp} values are given in Table 2.

In Fig. 5a, the experimental values of the swelling pressure P_t under the isochoric conditions are presented. Figure 5b shows the normalized experimental and calculated curves of the swelling pressure P_t/P_m versus the sorption time. Theoretical curves calculated from Eq. (9) at various values of relaxation rate constants k_{Rp} and the P_m values for different composites (see Table 2) are superimposed on the experimental dependences.

The good agreement of the experimental and theoretical values is observed. Introduction of SiO₂ phase into the composite leads to the decreasing of k_{Rp} , thereby the relaxation time of the polymer chains increases due to the formation of the double network structure of the hydrogels.

As it is shown in Fig. 5a the maximum value of the swelling pressure P_m is similar for all systems, while the time for its achievement is different. At the same time the maximum amount w_m of water absorption differs by more than an order that can be explained by different measurement regimes. Swelling of a greater amount of sorbate under isothermic conditions is determined by increasing of the dimensions of the sample and by the appearance of a free volume which is necessary for the placing of water molecules.

Fig. 5 a - kinetic dependences of the swelling pressure for composites with different SiO₂ content under the isochoric conditions; b - the experimental values of the normalized swelling pressure P_t/P_m (points) and the calculated kinetic curves arranged in accordance with Eq. (9) for samples with different SiO₂ content



The equilibrium value w_m in the isothermic regime is reached when the number of sorbate molecules appeared as a result of diffusion is balanced by the elastic properties of the stretched macromolecules of the matrix. Obviously, the value of w_m is determined by the nature of the intermolecular interactions, the elasticity and strength of the polymer network.

The intermolecular interactions of sorbate molecules with the constituents of the hydrogel, which are observed at the isochoric conditions, lead to the accumulation of a sorbate in a limited volume of the composite. The rearrangement of the molecular structure of the composite occurs under the action of water solvating molecules at the conditions of internal pressure. When the diffusion flow is stopped by internal pressure, the equilibrium ($P_i = P_m$) state establishes. Internal pressure prevents the appearance of a free volume for coming and stabilization of new sorbate molecules. At the same time, if strong intermolecular interactions in the system exist, this can lead to a break in the overstressed sections of the chains and, in general, to the destruction of the polymer structure. Indeed, as it is seen from Fig. 5a and b, after reaching P_m value, the internal pressure P_i decreases due to the destruction of the molecular structure. In PAM, this process begins much earlier, and drop of the swelling pressure is greater than for PAM/SiO₂ composites. This fact is explained by strengthening the molecular structure of the composite as a result of reinforcing the organic network by inorganic one.

Conclusion

The composite based on hydrophilic organic-inorganic PAM/SiO₂ networks with IPN structure were prepared by in situ polymerization of AM and SiO₂. The FTIR spectra and DSC analysis indicated the formation of network structure and confirmed decreasing of H-bonds quantity in PAM with SiO₂ content increasing due to formation of mixed PAM/SiO₂ phase. The experimental results of structuring of OIC hydrogels and intercomponent interaction by means of H-bonds indicate improvements in the thermal stability and swelling ratio. It was found that sorption of H₂O molecules both in isothermic and isochoric regimes corresponds to diffusion mechanism of Type II and is limited by relaxation of macrochains during swelling process of hydrogels. Enhanced sorption and consequently great volume of swelled water (for sample PAM/SiO₂ = 75/25 swelling degree is more than 2730%) is a result of structuring of OIC hydrogels.

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