

STRUCTURE AND SWELLING OF POLYMER-CLAY COMPOSITES

R.S. Iminova, Sh.N. Zhumagalieva, M.K. Beisebekov, Zh. A. Abilov, G.A. Mun

Al-Farabi Kazakh National University, Chemistry Department.

Chair of Organic Chemistry and Chemistry of Natural Compounds, Karassai batyr str.,95A, Almaty, Kazakhstan

Abstract

Composition gels on the basis of bentonite clay of Manrak deposit (East-Kazakhstan region) and nonionogenic polymers - poly-2-hydroxyethyl-acrylate and polyacrylamide were synthesized by radical intercalative polymerization in situ with various content of cross-linking agent N,N-methylene-bis-acrylamide and with time of intercalation about 8 hours. The morphological structure, the nature of interaction of components and the swelling ability of composition gels were studied by scanner electron microscopy, equilibrium swelling and IR- spectroscopy methods. By studying of morphological structure it was determined, that the polymer-clay composition gels, synthesized by intercalative polymerization, are most homogenous and interconsistency in case of "acrylamide-clay" composition in contrast with "2-hydroxyethylacrylate -clay" composition. For "acrylamide-clay" gels the swelling degree of gels was stated to decrease with the increase in the content of cross-linking agent and ionic strength, but "2-hydroxyethylacrylate -clay" compositions have the extremely character of swelling, where maximum degree of swelling account for gel with content of cross-linking agent $1 \cdot 10^{-2} \text{M}$. Interaction of composition components was realized on account of hydrogen bonds with formation of chemically cross-linked complex polymer-clay. Decrease of swelling degree of compositions in physiological solution points to acquisition of polyelectrolyte nature of composition gels on account of combination of nonionogenic macromolecules of polymers with negatively charged particles of bentonite clay. For intercalated samples of polymer-clay compositions, the degree of swelling at all degrees of cross-linking is between those for pure polymers and pure clay, that in turn, agrees with the conclusion on the great composition homogeneity of samples with preliminary intercalation. As of results of holding investigation fit is safe to say, that obtained polymer-clay composition gels are potential sorbents and prolonged carriers of medicines.

Introduction

At the present stage of development of industry branches related to production and consumption of sorbents as well as the field of medicine dealing with creation of prolongation carriers of medicinal substances, it is necessary to search for more available fillers, the introduction of which into polymer would not only make them cheaper but also increase there physico-chemical, sorption-desorption and mechanical properties [1, 2]. From this point of view, special attention of investigators has been attracted lately by polymer-clay systems on the basis of ionogenic and nonionogenic polymers and layers silicates, in particular, bentonite clays with high content of mineral – montmorillonite [3, 4]. Compositions on the basis of silicates

realize some positive properties of composition components. Two major findings have stimulated the revival of interest in these materials: first, the report from the Toyota research group of a Nylon-6 (N6)/montmorillonite (MMT) nanocomposite, for which very small amounts of layered silicate loadings resulted in pronounced improvements of thermal and mechanical properties; and second, the observation by Vaia et al. that it is possible to melt-mix polymers with layered silicates, without the use of organic solvents. Today, efforts are being conducted globally, using almost all types of polymer matrices.

One of the methods of obtaining composition materials is radical intercalation polymerization in situ of polymers on the surface of clay fillers [5, 6]. This method has been used since 1960 and continues to be in mass, solution, emulsion or suspension [7]. The process of monomer polymerization takes place in the interlayer space of clay structure (montmorillonite) [8]. The advantage of this method

*corresponding author. E-mail: riza_529@mail.ru

is that, if polymerization proceeds inside galleries, particles of clay will gradually swell and, finally, exfoliate into discrete layers. Synthetic polymers, such as polyacrylamide, polycarbonic acids, polyhydroxyethylacrylates and others may serve as the continuous phase in composites. Besides, clayey materials initiate or inhibit numerous reactions of polymerization and indirectly influence the process changing its direction, thereby producing composition systems with modified structure and new properties [9, 10].

The object of this work is synthesis and investigation of the morphological structure and swelling ability of composite gels on the basis of cross-linked nonionogenic polymers, such as polyacrylamide (PAA) and poly-2-hydroxyethylacrylate (PHEA) with included dispersion of particles of bentonite clay of Manrak deposit (East-Kazakhstan region).

Experimental

Materials

The following reagents: bentonite clay (BC) of Manrak deposit of East-Kazakhstan region, acrylamide (AA) («Reanal», Hungary), 2-hydroxyethylacrylate (HEA) of the firm «Aldrich Chemical Co., USA», a cross-linking agent – N,N-methylene-bis-acrylamide of Belgium production, (MBAA) of analytical grade, an initiator – potassium peroxydisulphate (PPS) were used in the work.

Chemical composition of natural and purified bentonite clays was determined by the method of diffraction spectral analysis (Table 1) [11].

According to the results of X-ray phase analysis (DRON-4-07), in the bentonite clay being studied three phases: α -quartz - SiO_2 , montmorillonite-

$\text{Al}_2[\text{OH}]_2\{\text{Si}_4\text{O}_{10}\} \cdot m\text{H}_2\text{O}$ and amorphous phase were determined.

Synthesis of polymer-clay composition gels HEA-BC and AA-BC

Intercalated compositions were synthesized by radical intercalation polymerization in situ in monomer solution in aqueous medium with included dispersion of bentonite clay with different contents of the cross-linking agent. The suspension of bentonite clay in water was prepared by mixing on magnetic mixer during 2 hours. Then a monomer was added to suspension and continued mixing it during 6 hours more. Then the suspension was heated to 40 °C and cross-linking agent and initiator were added to it. After that the suspension was poured into ampoules with the diameter of 3 mm, the test tubes were isolated against air by a laboratory film. The content of the cross-linking agent was varied within 0.05-1 mol. % of the monomer weight, and for HEA-BC – $5 \cdot 10^{-3}$; $1 \cdot 10^{-2}$; $2 \cdot 10^{-2}$; $5 \cdot 10^{-2}$; $1 \cdot 10^{-1}$ M, the concentration of the initiator in compositions makes up 1 mol. % of the monomer content. Copolymerization of AA-BC was carried out during two hours at 40 °C, and in case of HEA-BC – at 60 °C and then during 20 hours at 25 °C in an air thermostat [12].

The obtained gels were washed out from the unreacted monomers with distilled water. The completeness of washing of composites gels was controlled by a qualitative reaction with bromine water in case of gels HEA-BC, and in case of AA-BC – by a qualitative reaction for an amide group [13].

The obtained gels were dried under vacuum at 70 °C to the constant weight. Fractions with the size of particles < 0,1 mm were taken for experiments.

Table 1.

Chemical composition of natural and purified bentonite clays

Clay sample	The contents of components, %								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	H ₂ O	Loss after anneal
Natural	65	13	1	0.5	1.5	1.5	0.5	11	6.5
Purified	60	9	0.5	0.5	1	0.8	0.5	7	20.3

The Methods of investigation

IR-spectroscopy

For all synthesized polymer-clay gels as well as for initial substances, IR-spectra were taken on the spectrophotometer with Fourier transformation «FT/R Satellite» of the film «Mattson» (USA) using KBr.

Scanning electron microscopy (SEM)

The morphology and structure of all composition gels were studied with the help of images taken on the scanning electron microscope JEOL JSM-6380A with EDS-detector (Japan). The samples were placed into tubes and gold-coated in Quick Auto Coater, and then studied at 15-20 kV.

Swelling degree

The swelling degree was determined gravimetrically and calculated by the ratio of the mass of the swollen sample to the mass of the dry sample by formula [14]:

$$\alpha = m - m_0 / m_0$$

where, m_0 is mass of the dry sample,
 m is mass of the swollen sample.

Results and Discussion

Synthesis of polymer-clay composition gels gives the possibility to combine valuable chemical, physical and mechanical properties which a characteristic of the initial components: unotoxicity, complex forming ability, swelling and sorption abilities, mechanical strength, and chemical stability. At the same time, to create composition materials of the required quality, it is necessary to study the nature of interaction and the character of binding of initial components in the composition.

Being an inorganic mineral polymer, bentonite clay has a complex chemical structure which mainly consists of negatively charged particles with tetrahedral and octahedral OH-groups showing a tendency to hydrogen bonds. Figure 1 presents IR-spectrum of purified bentonite clay where one may observe a rather strong doublet at 470-526 cm^{-1} , which is characteristic of montmorillonite. The absorption band at 915 cm^{-1} is characterized by vibrations of Al-OH bond. Maximum in the range of

1038 cm^{-1} refers to asymmetric stretching vibrations of Si-O. Stretching vibrations of structural OH-groups are observed in the form of a wide absorption band at 3629 and 3447 cm^{-1} . In a whole, IR-spectrum of clay indicates a low degree of perfection of the structure.

The spectra of polymer-clay compositions (Figure 1) clearly show characteristic bands referring to the initial components. So, polymers PHEA and PAA contain complex ether and hydroxyl groups (PHEA) and NH_2 -group (PAA) tending to hydrogen bonds. The figure presents comparative spectra of pure polymers their compositions with clay, where is observed some difference. The spectrum of composition gels HEA-BC registers at 3600-3000 cm^{-1} gently sloping, wide, weakly intensive bands characteristic for interaction of OH-group of polymer and bentonite clay; OH-groups shifted by hydrogen, chelate bonds are registered in the range of 2874 and 2921 cm^{-1} .

Stretching vibrations of the complex ether group are registered in the range of 1726 cm^{-1} , deformation vibrations of Al-OH-group of clay are observed in the range of 916 cm^{-1} . The spectra also characterized by the presence of absorption bands of asymmetric bonds Si-O-Si in the range of 1037 cm^{-1} and deformation vibrations of Si-O at 671, 585, 475 cm^{-1} .

IR-spectra of PAA-BC compositions show wide absorption bands in the range of 2785 cm^{-1} and 3700 cm^{-1} , characteristic for stretching vibrations of NH_2 -groups of PAA shifted to the short wave range as a result of disturbance by hydrogen bonds (Figure 1). Stretching vibrations of carbamide bonds are shifted, too, and are registered at 1671, 1490, 1417, 1452 cm^{-1} ; C-N bonds at 1356 cm^{-1} ; C-C aliphatic bonds at 1172, 1119 cm^{-1} . There appear asymmetric vibrations of Si-O-Si bonds at 1042 cm^{-1} with gypsum chromic shift of deformation vibrations of OH and Si-O bonds at 712, 670 cm^{-1} , respectively. In a whole, it may be concluded that binding of macromolecules of nonionogenic polymers with clay particles is realized completely on account of hydrogen bonds.

When studying of properties of the obtained nanocomposites, special attention should be paid to the study of distribution of the clay in the composite and the morphology of structure. According to the works of Giannelis [15, 16] the process of formation of a nanocomposite proceeds via a number of intermediate stages. At the first stage there takes place the formation of a tactoid - the polymer surrounds

agglomerates of organoclay. At the second stage, the polymer penetrates into the interlayer space of organoclay resulting in drawing the layers apart up to 2-3 nm. At the third stage, partial separation and disorientation of organoclay layers are transpired. At the last stage, there takes place shelling.

Actually, in the obtained polymer nanocomposites, all the mentioned structures may be presented, this

depending on the degree of distribution of organoclay in a polymer matrix. The shelled structure is the result of a very good degree of distribution. With the excess of clay and poor degree of dispersion, agglomerates of clay may be present in a polymer matrix. We have studied formation of the structure of the compositions being investigated by the method of scanning electron microscopy, the results

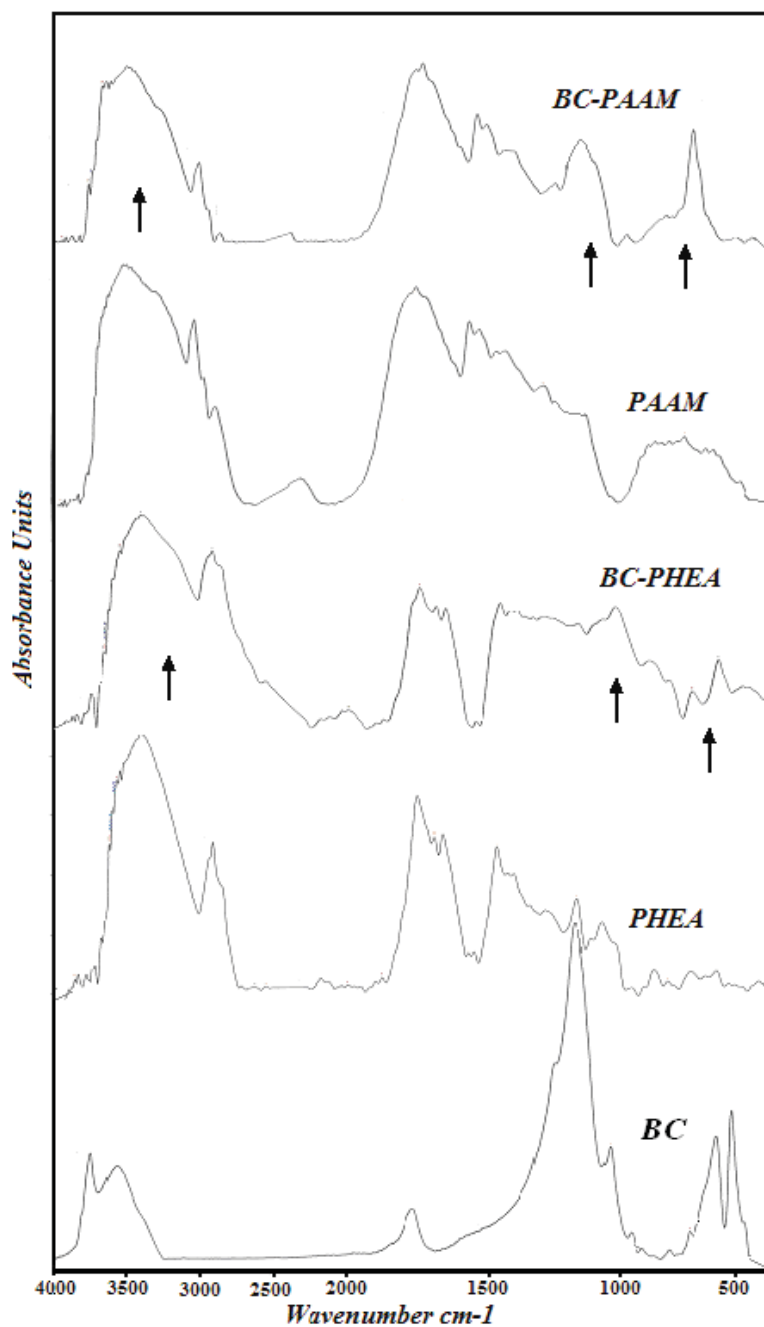


Fig. 1. IR-spectra

of which are presented in Figure 2. As is seen from the elemental analysis of SEM image in Figure 2 (A), pure bentonite clay used by us has a natural flaky laminated structure, and its main composition is that of silicon, aluminium and magnesium oxides. As during synthesis intercalation polymerization in situ was used, one may expect the formation of intercalated samples of the obtained compositions.

Indeed, in case of AA-BC system, one may observe a smooth surface with uniform distribution of clay platelets in a polymer matrix of PAA and penetration of monomers into interlayer space of clay, as can be seen in the image of the cross-section of the samples (Figure 2 (C)). However, composition HEA-BC is characterized by formation of large agglomerates of clay particles no uniformly dispersed in the matrix

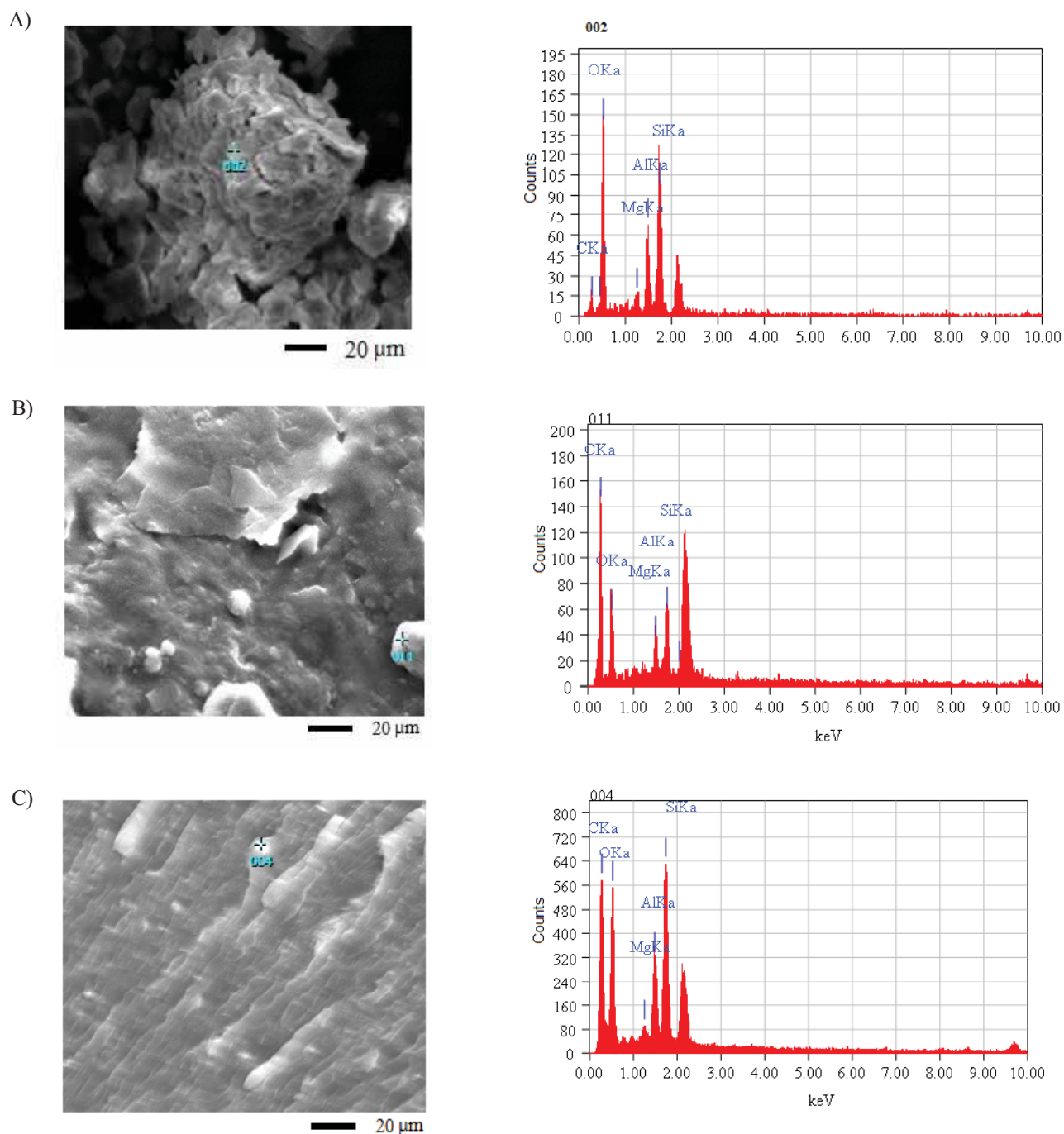
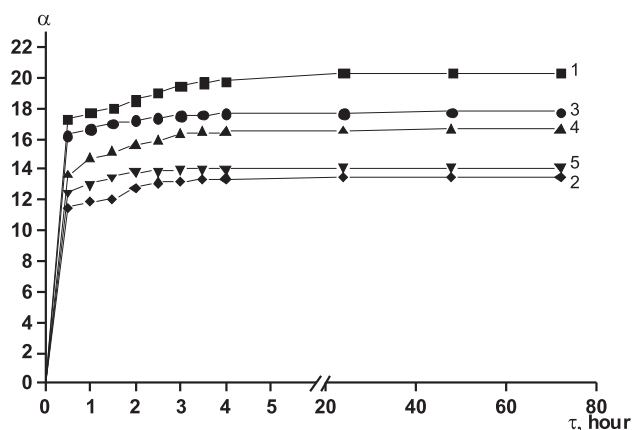


Fig. 2. SEM images of the surface of bentonite clay (A) and cross-section of nanocomposites: HEA-BC (B), AA-BC (C).

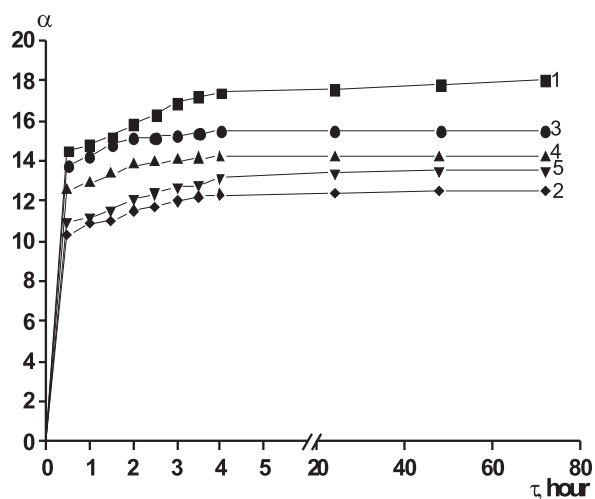
resulting in some roughness of the surface and the cross-section of the composition. This may be related to the amorphous state of polymer gel PHEA (Figure 2 (B)).

Among physico-chemical properties of polymer



PAA - (1); clay - (2); composites AA-BC (3-5); [MBAA]= 0,25 mol.% - (3); 0,5 mol.% - (4); 1mol.% - (5).

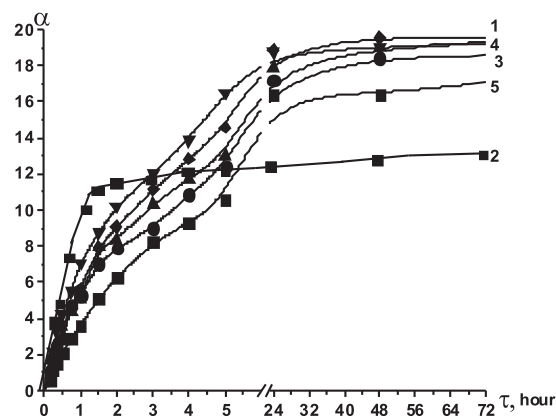
Fig. 3. Kinetics of swelling of composite gels AA-BC in water.



BC - (1); PAA - (2); composites AA-BC (3-5); [MBAA]= 0,25 mol.% - (3); 0,5 mol.% - (4); 1mol.% - (5)

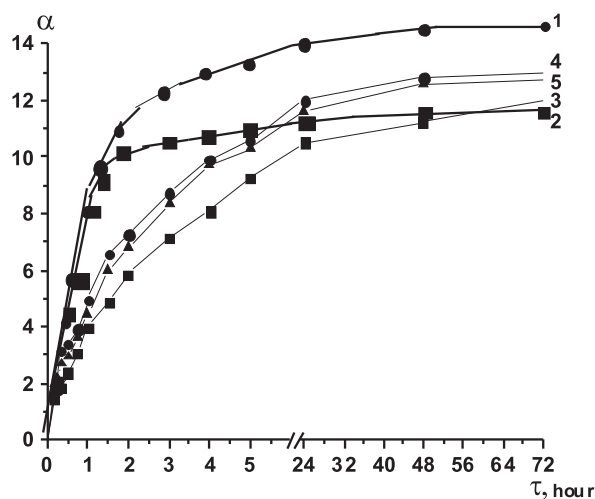
Fig. 5. Kinetics of swelling of composite gels AA-BC in physiological solution.

gels, of special interest is swelling of the gels which is very important when using them in biotechnology, food industry and medicine. The results of investigation on the swelling ability of composition AA-BC and HEA-BC are presented in Figures 3-6.



PHEA - (1); clay - (2); composites PHEA-BC(3-5); [MBAA]= 5×10^{-3} (3); 1×10^{-2} (4); 1×10^{-1} mol (5) [H₂O:HEA]=[90:10], [BC]= 9% against the monomer content

Fig. 4. Kinetics of swelling of composite gels HEA-BC in water.



PHEA - (1); clay - (2); composites HEA-BC (3-5) [MBAA]= 5×10^{-3} (3); 1×10^{-2} (4); 1×10^{-1} mol (5) [H₂O:HEA]=[90:10], [BC]= 9% against the monomer content.

Fig. 6. Kinetics of swelling of composite gels PHEA-BC in physiological solution.

for all samples of AA-BC, the swelling ability of compositions decreases with the increase of the content of a cross-linking agent (Figure 3) which is related to the increase in density of cross-linking and is in good agreement with the common regularities for cross-linked polymers. And composition HEA-BC is characterized by some optimum value of the cross-linking agent relative to the swelling ability. As is seen in Figure 4, maximum is observed with the amount of the cross-linking agent $1 \cdot 10^{-2}$ mol. %, then with the increase in the content of the cross-linking agent the swelling ability monotonically decreases. A disordered structure is likely to form as a result of a gel-effect in case of the lowest concentration of MBAA $5 \cdot 10^{-3}$ mol. % due to the lack of the cross-linking agent for formation of a cross-linked structure, and the cross-linking agent in the amount of $1 \cdot 10^{-2}$ mol. % creating an ordered cross-linked structure forms a gel with a high swelling ability.

The further decrease of swelling is a natural phenomenon – the increase in the density of cross-linking decreases the swelling degree of gels.

Comparing swelling of all samples in a whole, it should be noted that for intercalated samples of compositions polymer-clay, the degree of swelling at all degrees of cross-linking is between those for pure polymers (PAA, PHEA) and pure clay. This agrees with the conclusion on the great composition homogeneity of samples with preliminary intercalation.

Of great interest is the effect of ionic strength on these systems. In these connection, the swelling ability of gels in physiological solution (0,86% NaCl, Figures 5,6) was studied. The decrease of the swelling degree of compositions AA-BC and HEA-BC is observed from ~ 20 in water and up to ~ 13 in physiological solution. These changes taking place under the effect of ionic strength indicate the fact that composition gels acquire a polyelectrolyte nature [17] on account of combination of nonionogenic macromolecules of PHEA and PAA with negatively charged particles of BC.

Conclusions

Thus, the results of investigations allow to conclude that interaction between polymer and clay in composites takes place mainly on account of hydrogen bonds as well as hydrophobic interactions of hydrophobic chains of polymer due to which a chemically cross-linked complex polymer-clay is formed. The obtained intercompatible,

interpenetrating and homogeneous composition gels on the basis of PHEA, PAA and bentonite clay with a good swelling ability are of interest as prolongation carriers which requires further investigation of these systems.

References

1. Lomakin S.M., Zaikov G.E. Polymer nanocomposites of decreased combustibility on the basis of layer silicates. *Vysokomol. soed., Series B*, (2005), Volume 47, №1, pp. 104-120
2. Pomogailo A. D. Synthesis and intercalation chemistry of hybrid organic-inorganic nanocomposites. *Vysokomol. soed., Series C*, (2006), Volume 48, №7, pp. 1318-1351
3. Goettler L.A., Lee K.Y., and Thakkar H. Layered Silicate Reinforced Polymer Nanocomposites: Development and Applications. *J. of Polymer Reviews*, (2007), Volume 47, pp. 291-317
4. Iminova R.S., Kudaibergenova B. M., Zhmagalieva Sh.N., Beisebekov M.K., and Abilov Zh.A. Polymer composition materials. *Vestnik KazNU, Chemical series*, (2006), №1(41), pp. 61-71
5. Kun Xu, Jihua Wang, Sheng Xiang, Qiang Chen, Wende Zhang and Pixin Wang Study on the synthesis and performance of hydrogels with ionic monomers and montmorillonite. *Applied Clay Science*, (2007), Volume 38, Issues 1-2, pp. 139-145
6. Se-Hoon Kim¹, Sang-Hyun Park¹, Sung-Chul Kim Novel clay treatment and preparation of Poly(ethylene terephthalate)/clay nanocomposite by In-situ polymerization. *Polymer Bulletin* 53, (2005), pp. 285–292
7. Lisa M. Stadtmueller, Kyle R. Ratinac and Simon P. Ringer The effects of intragallery polymerization on the structure of PMMA–clay nanocomposites. *Polymer*, (2005), Volume 46, Issue 23, pp. 9574-9584
8. Wei'an Zhang, Yu Li, Luo Wei and Yue'e Fang In situ intercalative polymerization of poly(methyl methacrylate)/clay nanocomposites by γ -ray irradiation. *Materials Letters*, (2003), Volume 57, Issues 22-23, , pp. 3366-3370
9. Ivanchev S.S., Dmitrienko A. V. Polymerization filling by the method of radical polymerization as a method of obtaining composition materials. *Uspehi Himii*, (1982), Volume 51, Issue 6, pp. 1178-1200
10. Akimbaeva A.M. Successes and problems in

- the field of polymerization of monomers on the surface of disperse layer silicates. Izvestia of NAS of RK, Chemical series, (2003), №3, pp. 84-96
11. Zhumagalieva Sh.N., Beisebekov M.K., Abilov Zh.A., Akhmedova Sh. S. On bentonites and their usage in medicine. Vestnik KazNU, Chemical series, (2001), №3 (23), pp. 41-50
 12. Essikova O.V., Starodubtsev S.G., Khokhlov A.R. Synthesis, swelling and absorption properties of composites on the basis of polyacrylamide gel and sodium bentonite. Vysokomol. soed., Series A, (2002), Volume 44, №5, pp. 802-808
 13. Beisebekov M.K. Beisebekov M.K. Polymer derivatives of medicinal and biologically active substances. Kandidatskaya dissertaciya, 2004, Almaty, P. 52
 14. Kuznetsov E.V., Divgun S.M., Budarina A.A., Avakumova N.I., Kurenkov V.F. Practical work on physics and chemistry of polymers. –M.: Chemistry, 1977, 256 p.
 15. Giannelis E.P., Polymer-layered silicate nanocomposites: synthesis, properties and applications. Appl Organomet Chem, (1998), Volume 12, pp. 675-680
 16. Mikitaev A. K., Kalajan A.A., Lednev O.B., Mikitaev M.A. Nanocomposite materials on the basis of organoclays. Electron journal «Issledovano v Rossii», 2004, pp. 912-921
 17. Iminova R.S., Zhumagalieva Sh.N., Beisebekov M.K., Mun G.A., Abilov Zh.A. Synthesis and investigation of composition gels on the basis of 2-hydroxy-ethyl-acrylate and bentonite clay. Proceedings of the II Inter. Sci. Conf. “Chemistry, technology and medical aspects of natural compounds”, 2007, Almaty, Kazakhstan, P.301.

Received 19 february 2009.