American Journal of Polymer Science 2017, 7(2): 38-43
DOI: 10.5923/j.ajps.20170702.03

Polymeric Compositions on the Base of Acrylic Acid and Bentonite Clay

M. A. Mahkamov*, M. G. Muhkamediev

Department of Chemistry, National University of Uzbekistan, Tashkent, Uzbekistan

Abstract In this investigations some peculiarities of obtaining composition hydrogels (CH) on the base of cross-linked polyacrylic acid (PAAc) and bentonite clay (BC) were investigated. Optical microscopy and X ray diffraction have shown that in CH's destruction of crystalline structure of montmorillonite has carried out owing to penetrative of polymeric macromolecules between bundle layers in result of which CHs have a uniform homogeneous structure. The kinetics of swelling of obtained CH in water was investigated and it was shown that they have a high sorption ability to water in wide interval of pH. Sorption of methylene blue (MB) by gels from water solutions was investigated by statistical method. It was determined that sorption ability of CHs was higher than by hydrogels on the base of PAAc. Sorption of MB has increased with increasing temperature of medium and consequently the bonding of MB by CHs has carried out owing to chemisorption.

Keywords Acrylic acid, Bentonite, Composition hydrogel, Swelling, Sorption

1. Introduction

Polymeric hydrogels (PH) are objects of practical interest owing to possibilities of their using in many fields of science and industry for solutions of different problems. PHs can be used in medicine as medical compounds; for division and adsorption of ions of different metals; in ecology for purification of sewage from different organic and inorganic impurities; for obtaining sensors [1-7]. The base of PHs in most cases is synthetic polymers, distraction of which in natural conditions is difficult what is their lack from the point of ecology. By this reason construction of absorbents on the base of biodegradated materials and decreasing in their composition the content of synthetic polymers is one of the important task. The obtaining of compositions on the base of cross-linking polymers by introductions in their composition of different natural materials is one of possible ways of decision of this problem. By this reason polymer-bentonite compositions have the special interest. The choice of bentonite clay (BC) as component for polymeric compositions is determined by its high hydrophilicity, low toxicity, ecological safety; the good adsorption ability and also that it is accessible and cheap material. These properties of BC's have allowed to consider it as the most perspective material for obtaining composites. Authors [8, 9] have shown that BC particles have attached to gels some new phisico-chemical properties and also improved their mechanical properties. Therefore construction of composition hydrogels (CH) on the base of such system as polymer-BC and investigation their phisico-chemical properties have allowed to decide some problems arising at PHs using.

The aim of this work is synthesis of CHs on the base PAAc gel with inclusion of BC particles and investigation of some physico-chemical properties of obtained materials.

According to aim, PHs were obtained on the base of PAAc and CHs by radical polymerization of acrylic acid and cross-linking agent adsorbed on the BC. Investigation of the sorption degree of obtained materials was carried out. Sorption of methylene blue (MB) by synthesized materials from water solution in statistical condition was investigated for determination of their sorption ability.

* Corresponding author:
muz_m77@mail.ru (M. A. Mahkamov)
Published online at http://journal.sapub.org/ajps

2. Experimental

2.1. Chemicals

Acrylic acid (AAc; OAO Reactive, Russia) was vacuum distilled at 47°C/ 7mm Hg. The cross-linker N,N'-methylene-bisacrylamide (N,N'-MBAA; BDH Chemical Ltd, England) was of analytical grade. Methylene blue or methylthionimium chloride (MB, Russia) is a dye having also antiseptical properties. Bentonite clay (Uzbekistan) of grade "Navbahor" has following composition, mass %:

Name	SIO_2	TIO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	FeO	others
Alkali bentonite clay	57,91	0,35	13,69	5,10	1,84	0,48	1,53	1,75	0,43	0,75	-	16,71

and it before using was washed and dried on the air to constant mass and then was carefully reduced to fragments.

2.2. Synthesis of Hydrogels and Composition Materials

PHs were obtained by polymerization of acrylic acid (AAc) in water solution in the presence of cross-linking agent N,N'-MBAA. Oxidized-redoxy system on the base of thiosulfate sodium and persulfate potassium was used as initiator. Reaction was carried on at 25°C during 24 h. The obtained gels were placed in glass column and were washed by distillated water during 20 h and then were dried at temperature 45°C to constant mass.

For obtain of CH firstly the suspension of BC in water at mixing by magnet stirrer during 2 h was prepared. Than to this suspension the monomer and cross-linking agent (AAc+N,N'-MBAA) were added and the obtained system was mixing during 6 h. Than to suspension the oxidized-redoxy system was added and mixture was poured in test-tubes. The copolymerization was carried out during 20 h at 25°C. After copolymerization the obtained gels were extracted from test-tubes, then they were purified from residues of monomers by repeated washing in column by distillated water and were dried at temperature 45°C to constant mass. Conditions of obtain of some investigated systems are presented in Table 1.

Table 1. Conditions of obtain of the composition hydrogels on the base AAc-BC (according to mass ratio of initial mixture)

№ sample	[AAc], mass %	[BC], mass %	[AAc]:[BC], mass	[N,N'-MBAA], mass % from AAc mass
1	100	0	1:0	0,33
2	95	5	1:0,05	0,33
3	91	9	1:0,1	0,33
4	87	13	1:0,15	0,33
5	87	13	1:0,15	0,43
6	87	13	1:0,15	0,50
7	87	13	1:0,15	0,60
8	87	13	1:0,15	0,64
9	80	20	1:0,25	0,33
10	67	33	1:1	0,33
11	50	50	1:2	0,33
12	40	60	1:3	0,33
13	34	66	1:4	0,33

2.3. Investigations of Gels Rheology

Roentgenograms of gels samples and compositions were recorded on the DRON-3 (Russia) at wave length 1,54 A. Microphotographies of PHs and CHs samples were recorded on the optical microscope BIOLAM-6 (Russia).

2.4. Degree of Swelling

Swelling degree of PHs and CHs in water was determined by the gravimetric method in special cells supplied by net from nylon polymeric material. The values of the swelling degree of hydrogels (Q) were calculated by following formula:

$$Q = \frac{(M_s - M_d)}{M_d}$$

were: M_s and M_d – the masses of swelling and dry samples.

2.5. Sorption of Methylene Blue by Gels

Sorption of MB from water solutions of PHs and CHs was investigated by the spectrophotometric method. Samples of gels with equal mass were placed in water solutions of MB and through some intervals of time the optical density of solutions (D) was measured on the SF-46 (Russia) at wave length 500 nm. MB concentration in solutions was determined on the base of calibrated graphic in coordinates: concentration of MB in solution- optical density.

3. Results and Discussion

3.1. Obtain of Hydrogels and Investigation Their Rheological Parameters

It is known that bentonits are an minerals with high content of montmorillonite which has formed very small leafs and fiber like isolations. Investigation with using of electronic microscope has shown the presence in it some characteristical lamellar, petal-like crystals. Crystalline lattice of montmorillonite has an ability to expansion [11, 12], what is caused by it's atomic structure. If inside of lamellar bundles in montmorillonite there are covalent bonds then between bundles there are only weak strengths of Van-der-Vaals. By this reason water and other polar liquids can easily penetrate in space between the bundles and the expansion or swelling of montmorillonit lattice has carried out. This can caused to increasing of distance between bundles in several times. High changing capacity of the montmorillonite in comparison with some other clay minerals also can be explain by fact that in it's crystals the ionic exchange has carried out not only on the outer surface of crystals but also inside of the crystalline lattice between atomic layers. Correspondently at water sorption the swelling was carried out not only owing to formation of solvatic covers on the surface of bundles but also to introduction of water molecules between bundles of the crystalline lattice [13].

It is obvious in this case that at addition of monomers in BC suspensions their penetration can carried out between bundles layers of crystalline lattice of montmorillonite (Fig. 1.b).

At polymerization of some monomers the nettings are formed the cells of which are filled by BC crystals (Fig. 1.c). Such scheme of formation of the polymeric composition was presented in work [14].

Obtained in our work CHs were a porous homogeneous masses swelling in water. For investigation of the surface structure of the obtained CHs their microphotografies were obtained (Fig. 2).

As shown from Fig. 2.b particles of BC are presented as good distinguished black point in optical microphotography. On the microphotographies of CHs (Fig. 2.c; 2.d; 2.e; 2.f) particles of BC practically didn't differed. This fact is about distraction of bundle structure of the montmorillonite on the more small structures. Also it is shown that obtained CHs are homogeneous and they have the porous structure. Changing carrying out in structure of montmorillonite in process of CHs obtain have discovered in diffraction patterns which are presented in Fig. 3.

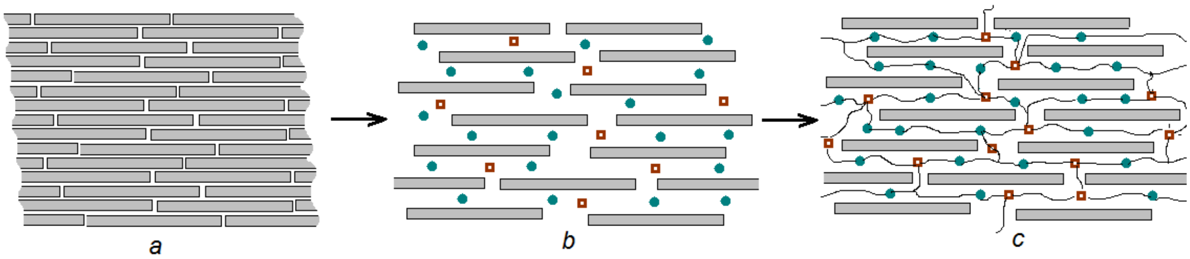

Figure 1. Scheme of the compositions hydrogels formation on the base of cross-linking PAAc and BC

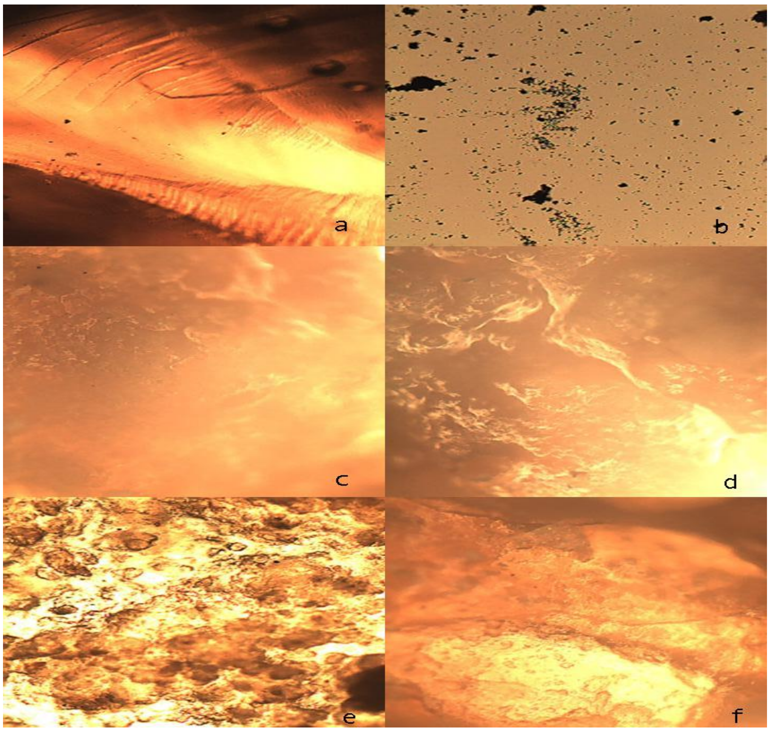

Figure 2. Microphotographies of the cross-linking gel on the base of PAAc (a); particles of BC (b) and CH (content of BC in composition: c-33; d-50; e -60 and f-66 mass %)

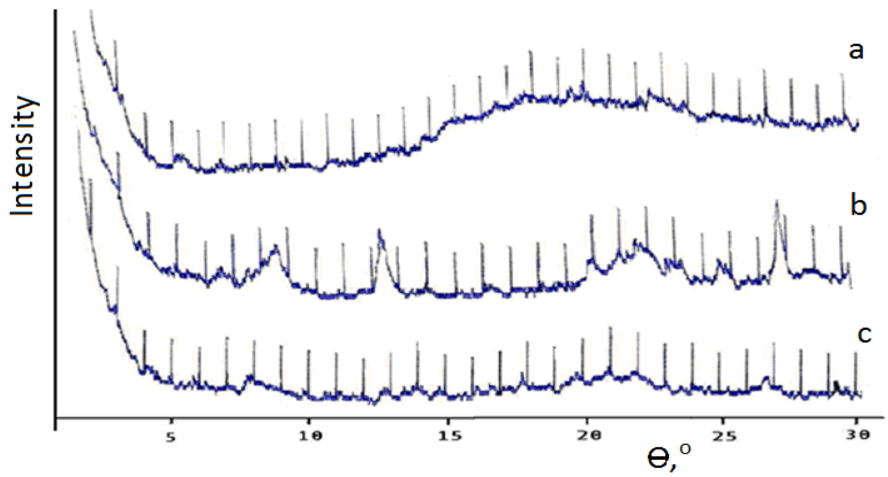

Figure 3. Diffraction patterns of gel samples on the base of PAAc (a), BC (b) and CH (c). Content BC in CH - 33 mass %)

As shown from Fig.3 in diffraction pattern of BC (Fig. 3.b) some crystalline reflexes at 20-22°; 8-9° and 12-13° are presented which is corresponded to the crystalline structure of montmorillonite. The diffraction patterns of the dry gels on the base of acrylic acid (Fig. 3.a) are corresponded to diffraction pattern of amorphous polymer and in it's some characteristic peaks, typical to crystalline parts, didn't presented. Also the peaks corresponded to crystalline parts of montmorillonite also didn't presented, what can be explain by distraction of it's crystalline structure.

3.2. Swelling of Obtained Materials

One of the important parameter of hydrophilic gels is their degree of swelling an by this reason kinetics of swelling of obtained materials in water solutions was investigated. In the case of CHs it was shown that the equilibrium at swelling of complexes has been achieved during 6-7 h (Fig. 4). The increasing of content N,N'-MBAA in gels has carried out to decreasing their swelling degree.

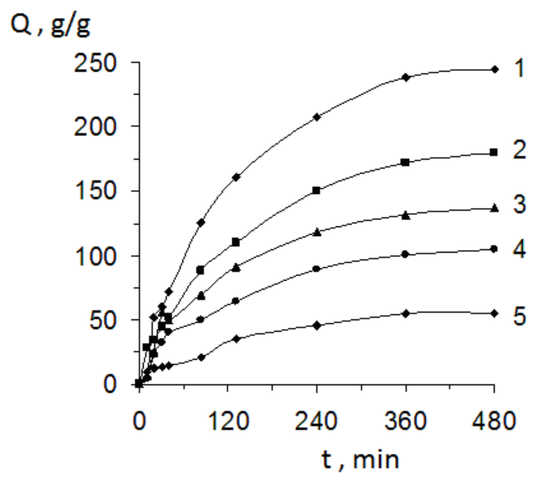

Figure 4. Kinetics of CHs swelling (content of BC -13 mass%) in water: 1,2,3,4,5-content of N,N'-MBAA in hydrogels correspondently: 0,33; 0,43; 0,50; 0,60; 0,64 mass % from of mass AAc; temperature 25°C

At investigation of BC content in obtained compositions on the degree of their swelling it was shown that dependence of the swelling degree of obtained CHs from content of BC in their composition has an extremal character.

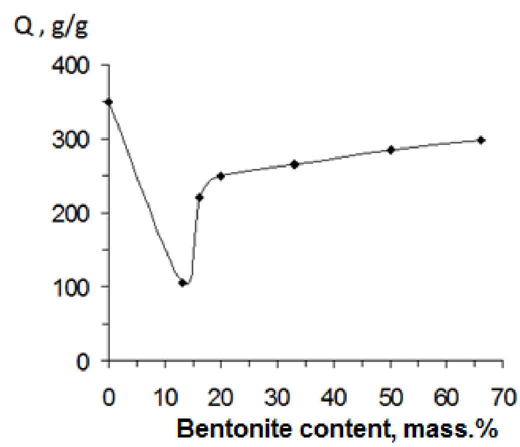

Figure 5. Dependence of the degree of equilibrium swelling of CHs from content BC in their composition (temperature 25°C)

It is shown (Fig.5.) that at small quantities of BC in CHs the swelling degree sharp decreased and then with it's increasing this parameter also contently increased. It is know that in BC there are cations of different metals mainly two valence (Ca^{2+}, Mg^{2+}). By this reason it is obviously that at small quantities of BC the additional cross-linking of gel through carboxylic groups by above-mentioned ions was proceeded in result of which it's the swelling degree decreased. The following increasing of BC content in CHs has caused to increasing of the swelling degree owing to swelling of BC containing in gel.

It is known that the swelling degree of gels with carboxylic functional groups depended on changing of pH medium and by this reason such gels are named pH-sensible [15, 16]. It was investigated the influence of pH of water solution on the swelling degree of obtained in this work polymeric materials. Water solutions with different values of pH were prepared by addition in water necessary quantities of NaOH or HCl.

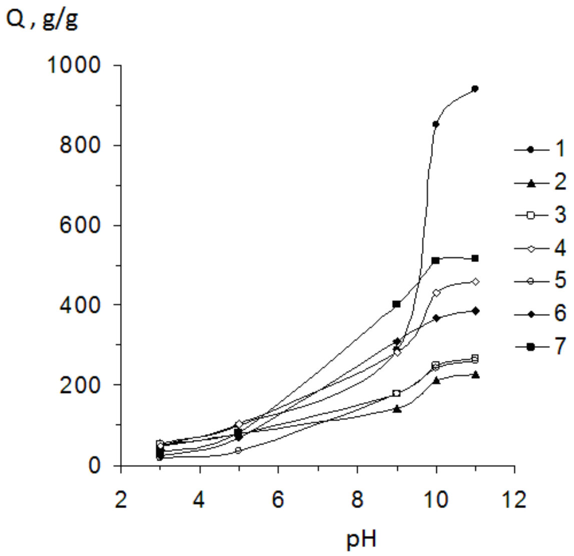

Figure 6. Influence of pH solution on the swelling degree of PHs and CHs. 1,2,3,4,5,6,7-content of BC in CHs correspondently equaled 0; 9; 13; 20; 50; 60 and 66 mass %. (temperature 25°C)

Degree of the equilibrium swelling of hydrogels on the base of PAAc has dependent from pH of water solution (Fig. 6, curve 1). In acid mediums they collapsided, but in alkali solutions they have maximal degree of swelling. In contrast to gels on the base of PAAc the swelling degree of CHs was less depended on changing of pH of solutions. Also it is necessary to note that with increasing of BC in polymeric gels their sensibility to pH changing has decreased.

3.3. Sorption

One of the important characteristics of PHs is their sorption ability in relation to different organic and inorganic compounds. By this reason absorption of MB from water solutions by obtained gels was investigated. Sorption of MB by hydrogels on the base of PAAc and CHs from water solutions was investigated in staticall conditions. Kinetics of MB sorption by polymeric material is presented on Fig. 7.

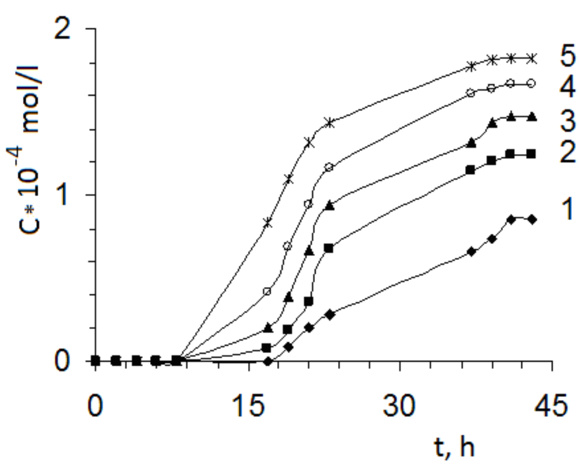

Figure 7. Kinetics of MB sorption (concentration 2·10^{-4} mol/l) from water solutions by polymeric materials: 1- polymer gels on the base of PAAc; 2,3,4,5 –CHs with BC content 33; 50; 60; 66 mass % correspondently

As shown from Fig. 7 sorption of MB by PH and CHs has begined through several hours after placing them in solution. Investigation has shown that sorption of MB by gels begined only after their equilibrium swelling in water. Introduction on BC in composition of gels caused increasing of their sorption ability. In CH containing 66 mass % of BC the sorption capacity was in two time more in comparison with the gel obtained on the base AAc. Also in all cases the sorption of MB by polymeric materials from solutions has carried out enough long time and equilibrium has ensued approximately through 40 h.

Investigation of MB sorption by gels on the base of PAAc and CHs at different temperatures has shown that sorption of MB from solutions increased with rising of temperature (Table 3).

Table 3. Influence of temperature on the quantity of sorbited MB by polymeric materials

Polymeric material	Quantity of sorbited MB, *10^{-4} mol/l		
	30°C	45°C	60°C
Gel on the base of PAAc	1,35	1,47	2,05
CH (content of BC 66 mass %)	2,43	2,55	2,80

This fact has indicated that sorption has an chemical character. Also in all cases MB sorption from solutions by CHs is more in comparison with gels on the base of PAAc.

4. Conclusions

Thus in this work CHs on the base PAAc and BC were obtained. It was shown that obtained materials have an homogeneous structure. Investigation of the swelling degree of CHs in water has shown that this parameter has depended on BC content. With increasing of BC content in gels their swelling degree firstly decreased and than constantly increased. Investigation of pH influence on the equilibrium degree of swelling had shown that with increasing of BC content in gels their sensitive to pH changing decreased. Sorption of MB by obtained sorbents was investigated and also it was shown that CHs possessed more sorption capacity in comparison with gels on the base of PAAc.

It was determined that sorption of MB has beginned after swelling of composition materials. The increasing of temperature has resulted in increasing of MB sorption which had a chemical character. Thus the possibility of obtain of effective absorbents on the base of composites PAAc-BC has been shown.

REFERENCES

[1] H. Omidian, J.G. Rocca, K. Park, J. of Controll. Release 102 (1) (2005) 3-12.

[2] S.K. Bajpai, Seema Dubey, Reactive & Functional Polymers 62 (2005) 93-104.

[3] H. El-Hamshary, M. El-Garawany, F.N. Assubaie, M. Al-Eid, J. Appl. Polym. Sci. 89 (9) (2003) 2522-2526.

[4] H. Bronsted, J. Kopecek, Polyelectrolyte Gels. Properties, Preparation and Application. Eds. Harland R.S., Prudhomme R.K. 1990. Amer. Chem. Soc., Washington DC, 285pp.

[5] Z. Hu, Y. Chen, Ch. Wang, Y. Zheng, Y. Li, Nature 393 (6681) (1998) 149-151.

[6] I.Z. Steinberg, A. Oplatka, A. Katchalsky, Nature 210 (6) (1966) 568-571.

[7] A. Richter, G. Paschew, S. Klatt, J. Lienig, K. Arndt, H. Adler, Sensors 8 (2008) 561-581.

[8] K. Xu, J. Wang, S. Xiang, Q. Chen, Y. Yue, X. Su, S. Song, P. Wang, Comp. Sci. Technol. 44 (15-16) (2007) 3480.

[9] N.A. Churochkina, S.G. Starodoubtsev, A.R. Khokhlov, Polym. Gels and Networks 6 (3-4) (1998) 205.

[10] D. Gao, R.B. Heimann, Polymer gels and Networks 1 (1993) 225.

[11] S.B. Hendricks, R.F. Nelson, L. D. Alexander, J. Amer. Chem. Soc. 62. (1963) 1940.

[12] A. V. Kiselev, J. Phys. Chem. 93 (1940) 452.

[13] Y. Fukushima, Clay and Clay Minerals 32 (4) (1984) 320-326.

[14] S. S. Ray, M. Okamoto, Prog. Polim. Sci. 28 (2003) 1539-1641.

[15] A. Khokhlov, G. Starodubtzev, V. Vasilevskaya, Adv. Polym. Sci. 109 (1993) 123-171.

[16] O.E. Phillipova, Polymer Sci. 42 (2) (2000) 208-228.