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Influence of concentration of filler on process gel formation in the composition on the basis of bentonites and acrylic copolymers

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ABSTRACT: There are compositions on basis of bentonites and acrylic copolymers are received. Dependence of influence of concentration of filler in the reactionary mixes for the period of the beginning gel formation is revealed: with increasing of bentonite in the polymeric matrix beginning time of gel formation increases. Particles of bentonite filler is made role of inhibitor of the process, that leads to fall of growth rate and increase in speed of breakage of the chain during radical polymerization at copolymer formation of acrylamide.

KEYWORDS: Bentonite clay, filler, acrylamide, styrene, copolymer, gel formation, composition, monomer, polymerization, microstructure.

I. INTRODUCTION

Today, acrylic copolymers are used in various industries. They are used as drug delivery systems, fluids, contact lenses, prostheses, etc. [1-3]. The main properties of hydrogels that determine their practical use are a high degree of swelling and good physical and mechanical properties. However, in practice, a high degree of swelling leads to a significant deterioration in mechanical properties, such as strength and elasticity. In addition, cross-linked polymers, with high water absorption in the swollen state, lose their shape, which is unacceptable in the manufacture of products. All this is a significant disadvantage for materials based on acrylic water-absorbing copolymers.

There are various ways to solve this problem. One of these methods is the creation of mineral-containing polymer compositions. As inorganic fillers, most often, use different types of clay, carbon or glass fillers [4].

The use of various types of clays as polymer matrix modifiers allows us to solve a range of tasks from increasing the deformation-strength characteristics to obtaining materials of a given geometric shape, which leads to the creation of a whole assortment of new "intelligent" polymer composite materials. In addition to giving the polymer matrix improved strength characteristics, it is necessary that the composites retain their sorption properties, therefore, one of the types of fillers that are used are bentonites.

Bentonites are clay-like substances that are a natural moisture absorbent. They are used as raw materials for drilling fluids, for wastewater treatment, in winemaking as clarifiers, etc. [5,6]. That is why, when introduced into the polymer composition, bentonite particles can not only strengthen the gel structure, but also increase the degree of swelling of the polymer matrix [4]. It is also known that bentonites sorb polyvalent metal ions from aqueous solutions of salts [7,8]. Therefore, the creation of polymer acrylic composites with predictable properties and devoid of the above disadvantages is relevant, which will expand the range of applications of water-absorbing materials.

II. MATERIALS AND RESEARCH METHODS

Polymeric materials filled with dispersed fillers belong to heterogeneous systems with a highly developed phase interface. In the main works, for example, works [4-6], the influence of small quantities from 0.5 to 4 masses was considered. % bentonite corresponds to the amount of fillers on the physicochemical characteristics of polymer composites.

In the presented work there was a greater amount of filler - up to 60 mass. %, due to the fact that the increase in density and heat resistance of new polymer composites with a slight decrease in the quality of the material.

These substances are clay minerals with a large amount of montmorillonite, which are layered aluminosilicate with a layer size of up to 1 nm and a lateral size of up to several tens of nm, which includes clay particles that include an acrylic polymer network, which improves mechanical properties and prevents collapse of the networks [7].

This work presents the results of studying the effect of the concentration of bentonite filler in the preparation of water-absorbing composite materials based on bentonite of the Navbahor deposit (Uzbekistan), as well as acrylamide and styrene monomers with subsequent copolymerization of a colloidal suspension in a concrete matrix medium [9-12].

III. RESULTS AND DISCUSSIONS

The synthesis of bentonite-containing acrylic compositions was carried out in an aqueous medium by radical intercalation polymerization of a mixture of monomer solutions: AA (acrylamide), partially neutralized, and CT. (styrene) - with bentonite particles of various concentrations. Figure 1 shows the dependence of the start time of gelation on the concentration of filler - bentonite clay.

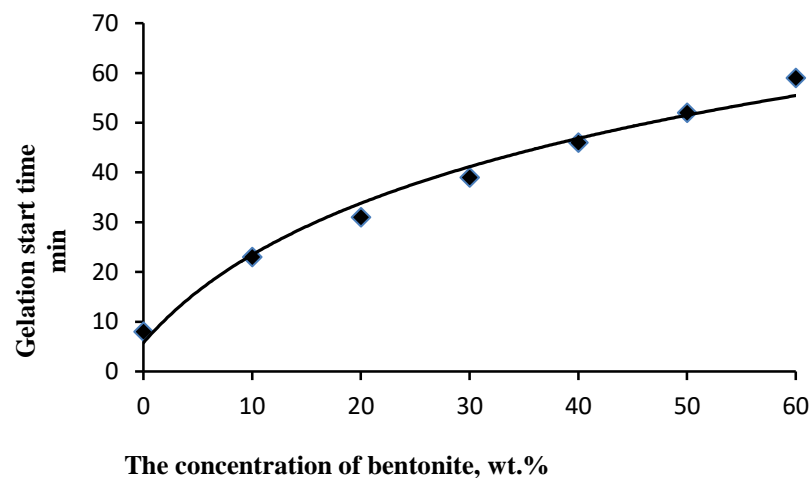


Fig. 1 Dependence of the start time of gelation during the synthesis of the composition on the concentration of bentonite.

Synthesis conditions: the synthesis time is 80 minutes, the synthesis temperature is 45 ° C, the concentration of MBAA (N, N'-methylene - bis - acrylamide) is 0.20 wt.%,

The proportion of monomers is 25 wt. %, monomer ratio: AA-65%, CT-35%, degree of neutralization AA-0.7, ammonium persulfate -1%.

As can be seen from Figure 1, the gelation onset time for systems filled with bentonite clay of any concentration is higher than for unfilled ones and is described by the following logarithmic equation:

$$\tau = 25,54 \ln[B] + 5,7523,$$

where [B] is the concentration of bentonite, wt.%, τ is the start time of gelation, min

The phenomenon of an increase in the start time of gelation with an increase in the fraction of bentonite can be explained by a decrease in the mobility of molecules in the adsorption layer on the surface of bentonite particles, which has a significant effect on the polymerization rate of macroradicals at the initial stage of the process. It is also possible to increase the start time of gelation due to the formation of hydrogen bonds between the monomer molecules and the functional groups of the filler.

On the other hand, as a result of isomorphic substitution, clay particles contain ions of various bi- and polyvalent metals, such as Ca^{2+} and Fe^{3+} , Ti^{2+} , Mg^{2+} , which significantly impede the radical polymerization of acrylic monomers. Thus, bentonite at the stage of initiation of the radical polymerization of acrylic monomers behaves as a moderator of the reaction, which was also observed earlier, as described in [4].

An important question posed in the study of the radical polymerization of bentonite-containing polymer compositions was the distribution of nanoparticles during synthesis in the polymer matrix. When conducting in situ intercalation polymerization, i.e. during the synthesis of a polymer carried out directly in the interlayer space of lamellar crystals, depending on the synthesis conditions, the formation of various nanocomposite structures is possible: from intercalated to exfoliated.

A similar dependence was observed for bentonite-containing composites synthesized on the basis of acrylic acid and methylene bisacrylamide, and described in [4]. The study of the swelling rate of polymer composites is one of the main tasks in creating moisture-absorbing materials, since in most cases it is necessary to quickly respond to

external influences. The absorption rate depends on the characteristics of the swellable polymer composition itself (degree of crosslinking, filler concentration, nature of the polymer matrix, etc.), and on external conditions such as temperature, pressure, nature of the environment, etc.

The table shows the kinetic characteristics of the swelling of polymer acrylic compositions with different proportions of bentonite.

Table 1

The dependence of the constant and the average swelling rate of bentonite-acrylic compositions in distilled water at a temperature of 25 ° C on the concentration of the filler.

Swelling rate constant, min ⁻¹	Speed in the initial section, g / h	The proportion of bentonite, mass. %
0,037	21,3	0
0,054	30,6	10
0,078	51,7	30
0,175	97,2	60

As can be seen from the table, with an increase in the proportion of filler in the polymer matrix, the swelling rate increases. Moreover, the speed at the initial site and the swelling rate constant for polymer bentonite-containing composites with a filler fraction of 60 mass. % increase by more than 4 times, compared with unfilled polymer.

When studying the behavior of ionogenic crosslinked copolymers in aqueous electrolyte solutions, most often, two modes of interaction of a hydrogel with polyvalent metal ions are considered in the case when the latter form water-insoluble compounds with reactive network groups:

- if the polymer concentration in the hydrogel-solution system is greater than the salt concentration, then the hydrogel absorbs predominantly pure water, increasing the salt concentration in the environment;
- if the polymer concentration is significantly lower than the salt concentration, then the hydrogel acts as an ion-exchange sorbent.

In order to study both modes in this work, we studied the effect of an aqueous solution of chromium chloride, taken in a concentration range of 10–5–10–2 mol/L, on the absorption properties of synthesized composite bentonite-containing materials.

The study of the surface of polymer - bentonite composites with different proportions of bentonite in the composition of the polymer composition was performed on a Phillips XL 30 transmission electron microscope and the obtained micrographs are presented in Figure 2.

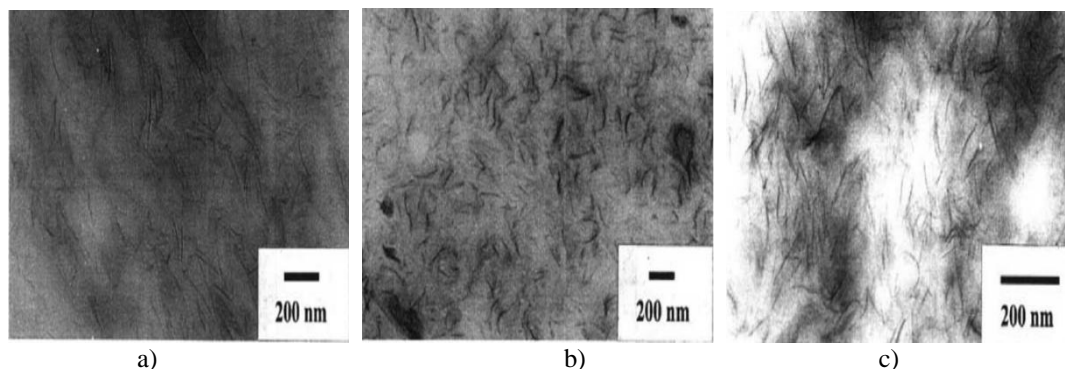


Fig. 2. Photos of the surface of composites based on acrylic copolymer and bentonite: a) unfilled copolymer; b) a composite with a concentration of bentonite of 10 wt.%; c) a composite with a concentration of bentonite of 40 wt.%.

As can be seen from Figure 2, when nanoparticles are introduced during the synthesis, a partially ordered structure such as a house of cards is obtained, which was also observed in [11] when studying the polymerization of acrylamide with bentonite in an aqueous medium at a synthesis temperature of 40 ° C during the day.

Table 2
Some parameters of polymer mesh

Share of active chains	Degree crosslinks	Density, g/sm ³	Moisture content, %	Share sol fractions,%	The proportion of bentonite, mass. %
0,56	2,62	1,11	43,6	8,4	0
0,51	2,34	1,14	63,4	9,3	5
0,52	2,39	1,17	51,7	10,2	10
0,44	1,98	1,21	35,2	13,7	30
0,36	1,69	1,26	41,9	16,9	40
0,35	1,65	1,32	32,8	17,8	60

In our case, complete exfoliation of plate crystals of bentonite in an acrylic polymer network was not observed, since for this it was necessary that the rate of radical polymerization of acrylic monomers inside the interlayer space of bentonite be higher than the rate of polymerization in the medium surrounding the filler particles or on its surface, which is possible only with effective intercalation of the catalyst or initiator in the interlayer space of the layered silicate and a sufficient diffusion rate of the monomers.

The main parameters of the grid characterizing the degree of crosslinking of the polymer include: the average molecular weight of the chain, the molecular weight of the crosslinking polymer, the number of chains of the grid and the number of crosslinking molecules, as well as the number and proportion of active chains and the degree of crosslinking. The results of the calculations, as well as some characteristics of the polymer composites are presented in the table.

As can be seen from the table, the increase in bentonite concentration leads to an increase in the share of the Sol fraction. This is due to the fact that the filler particles play the role of an inhibitor of the process, which leads to a decrease in the growth rate and an increase in the breakage rate of the chain during radical polymerization.

IV. CONCLUSION

It can be concluded that, as a result of the process, weakly crosslinked grids are formed in the formation of a composition of bentonites with a copolymer of acrylamide styrene, mainly of physical nature, which is confirmed by a large number of Sol-fractions, a decrease in the degree of crosslinking and the proportion of active chains carrying a load under various physical and mechanical influences.

From the above experimental data it follows that with an increase in the proportion of the filler in the polymer composition, the amount of chromium ions absorbed by the gel, and, consequently, the sorbent efficiency increases.

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