

Aluminosilicate microspheres as extenders of moisture superabsorbents

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Introduction

During late decades polymeric electrolyte hydrogels constituting of polymeric networks which are capable for hundredfold and thousandfold inturgescence and sensitive to external environment changes such as temperature, composition of solution, pH, pressure, lighting, etc., were subject to intensive scientific researches and have numerous applications within different industries, medicine, agriculture [1,2]. While application in industries absorbents may be used as desiccant material for very watered petroleum, oils, gasolines, drilling mud thickeners during mining operations and underground operations and streaming prevention in water saturated soils. In building industry they are used for manufacturing of polymer-concrete compositions with increased strength characteristics, while compositions with caoutchoucs and rubbers are excellent waterproof and water-retentive sealant materials. Moisture superabsorbents are used as well as effective sorbent of ions of heavy metals from industrial wastewaters, for water and ecological problem-solving, etc. Combination of high-level inturgescence with good mechanical properties, especially in turgent condition, has determinative significance in all these ranges of application.

However, common practice displays the opposite phenomenon: high-level inturgescence correspond to low mechanical properties, low resistance and elasticity of samples. Turgent polymers do not capable to keep geometric shape and therefore are impracticable for manufacturing of goods, that is material weakness of materials and technologies now available.

There are several methods of solution of this problem and creation of polymeric composite materials is one among them.

Principle of production of polymeric composite materials consists in creation of predetermined combination of two and more different phases (of extenders and matrix) using any technological methods. Polymeric materials having mechanical properties drastically differed from matrix characteristics are produced as a result of extension.

Essentially, this universal principle of creation of polymeric composite materials having new complex of physical and mechanical characteristics defined by system microheterogenicity and phasic interaction on boundary line of phases polymer-extender. In this case properties of composite material practically depend upon properties of extender to the same extent as of properties of initial polymer.

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One of the well-known and widely used extenders are aluminosilicate microspheres (ASM). Prospectivity of usage of non-organic extenders is spectacular in complex influence of aluminosilicate microspheres (ASM) upon the whole totality of performance parameters, including fire proofness.

For some practical applications it is desirable to use minimum level of extension because of essential importance of retention of physicochemical characteristics of cross-linked copolymers dispersion medium (e.g. gas permeability, adhesive contact endurance, etc.). One of the possible way for solution of this type problem is modification of polymers by fullerene (F) C₆₀ – i.e. production of nanocomposites. Theory of nanocomposites predicts the possibility of achievement of significant enhancement effect because of injection of microatomized matter modifying agents in number of 0.5% – 1.5% of weight share (mass percent).

Enhancement effect they are correlate with creation of supramolecular structures' physical net under impact of nanoparticles orienting influence. To date there were published rather numerous quantity of literature dedicated to polymeric materials, impregnated by nanodispersed particles of metals [3].

Scientific researches regarding creation of nanocomposites based upon cross-linked acrylate absorbents now practically absent and this situation is determined probably by the circumstance that the complex of physicochemical and strength characteristics of nanocomposites based on them are the results of unforecastable combined action of physical processes of self-organization (creation of hard blocks domens' physical nets and nanostructures, as well as of chemical three-dimensional network, created by cross-linking agent).

Experimental part

Extenders:

a) aluminosilicate microspheres:

Such properties of aluminosilicate microspheres (ASM) as spherical shape, low density, adequate strength, high adhesion to majority of polymers predetermine their wide use (see Table 1). Alongside with positive influence upon basic performance characteristics aluminosilicate microspheres (ASM) reduce shrinkage effect, decrease viscosity of compositions in comparison with geometrically unshaped particles of other extenders, increase antifricition and thermo-insulating characteristics, impact toughness and rigidness of goods [4].

Aluminosilicate microspheres (ASM) are widely used in extension of thermal barrier paints, automobile noise-eliminating coatings and mastic resins, lightweight refractory materials, as well as for manufacturing of composite polymeric heat-shielding materials and high-temperature densifiers, polymeric compositions for electronics and light constructional materials for airspace and shipbuilding machinery, etc.[5, 6].

Table 1 – Physical characteristics of aluminosilicate microspheres

Density of cover, g/sm ³	2.2÷2.7
Density of separate particle, g/sm ³	0.4÷0.8
Bulk density, g/sm ³	0.25÷0.5
Grain size, mcm	40÷500
Thermal conductivity, W/m×K	0.03÷0.04
Fusing temperature, K	1400÷1550
Specific heat capacity, joule/(kg×K)	750÷800
Hydrostatical durability (destruction level - 50%), MPa	30
Critical concentration of extension on volume basis, %	68

b) fullerenes:

This contribution have scrutinized the simplest of stable fullerenes - C₆₀, named as fullerite which has face-centered cubic lattice and density equal to 1.68 g/sm³.

According numerous investigations implemented during recent years, physicochemical properties of nanodimensional structures differ from both properties of separate atoms and molecules and properties of massive bodies, consisting of huge quantity of atoms or molecules. Assignment of regularities of consolidation of atoms and molecules into nanodimensional clusters, complexes and aggregations and ability to control the conditions of such consolidation should allow to create large quantity of new nanostructures, to investigate new phenomena and properties, distinctive in particular for nanoobjects and to create new functional materials and devices upon this basis.

Applications of F and their derivatives are rather wide: electronic and optical devices, delimiters of laser emission of visible and proximate intervals; additives to liquid lubricants, hard-oiling coverings; photographic materials and materials for transformation of electrical energy into light energy; catalytic agents and sorbents; nonlinear optics materials, etc.[7,8]. High strength properties, subject to molecular composition, allow to use F as boosting modifying agents during manufacturing of high-tensile composites.

Method of synthesis and investigation of characteristics of composite materials

Compositions based upon acrylate polymers and extenders, viz. aluminosilicate microspheres and fullerene were synthesized by radical aqueous polymerization under temperature of 20°C – 60°C. Reduction-oxidation system - ammonium persulphate (APS) - tetramethylethylenediamine was used as initiating agent, and N,N' – methylenebisacrylamide (MBAA) – was used as crosslinking agent. Neutralization degree of acrylic acid (AA) varied within interval $\alpha = 0.0 - 0.9$.

Polymerization was performed under initial concentration of monomer equal to 10-40 mass percent of acrylic acid weight, fullerene in number of 0÷0.5 mass percent and aluminosilicate fullerenes of 0÷60 mass percent for loading of monomers.

Characteristics and forms of chemical agents treatment, as well as procedure of process and investigation of synthesized materials properties are specified in contribution [9]. Composition synthesis time is 0.5 – 10 hrs. Fullerene was injected into reaction mixture without preliminary solubilization during initial phase of synthesis in admixture. As far as composition is heterogenetic thus determination of share of modifying agent – fullerene, not included into composition, was performed by gravimetric method after inturgescence of composition in distilled water during 5-7 days.

Consideration of results

Subject to conditions of synthesis – temperature, reaction time, extenders, concentration of initiator and monomer - in initial mixture may be derived absorbing substances and compositions with different physicochemical properties based upon them. Therefore, in specified contribution there were investigated the influence of abovementioned factors upon the properties of derived acrylic hydrogel compositions. Loading of extender results in augmentation of specific surface and pore volume, giving evidence of decrease of package density and thus about strong influence of extender upon structurization process and characteristics of the samples derived.

During formation of three-dimensional network of polymer the polymerization process in the presence of extenders proceeds in another way than in the absence of phase boundary. The presence of highly developed surface of extender results to speed increase of reaction net interruption on the surface of extender resulting to the reduction of lattice density and therefore, to its higher defectiveness. Because of absorption of growing polymeric chains the significant immobilization results and impacts upon both rate of propagation and speed of chain interruption, and therefore promoting more defective structure of polymeric matrix.

Figure 1 illustrates the dependence of gelatinization starting time (GST) on extender concentration - aluminosilicate microspheres (ASM) in polymeric composition. As it is evidently, GST of composites is more than GST of uncompounded systems and has extreme character.

Generally, we may suppose that immobilization of macromolecules in adsorption layer results in decrease of polymerization rate at initial phase of process. Apparently, during formation of interlaced polymers at initial stages of process up to 50% conversion there are created large branched molecules, characterized by limited set of conformations and considerably lower mobility, resulting in limitation of capacity of reactive groups to react and therefore the creation of interlaced polymer becomes slower.

Increment of gelatinization starting time (GST) may be explained as well by creation of hydrogen bonds between functionalities of monomer and extender. Reducing of gelatinization starting time (GST) together with increase of content of extender may be explained by internal reallocation and intermolecular bonds within reaction system.

Abovementioned results demonstrate that heterogeneity considerably impacts upon initiation mechanism and polymerization kinetics. It may safely be said that polymerization in barrier layer proceeds with higher speed than the same one in the volume and affects essentially on distribution of correlation of rate of propagation and chain interruption.

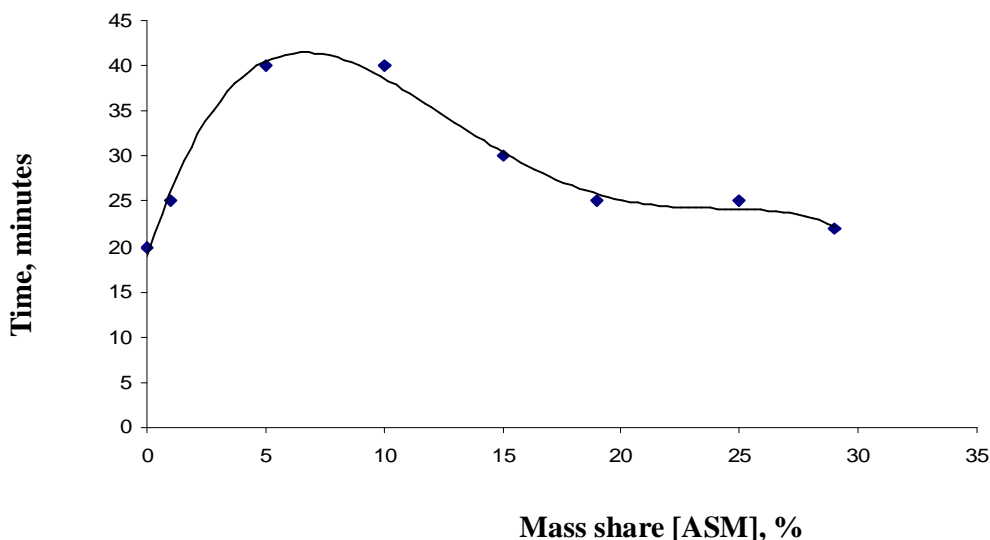


Figure 1 – Dependence of GST upon ASM concentration in polymeric matrix

Conditions of composition synthesis:

mass share, %: [AA] – 22; [MBAA] – 0.1; [PSA] – 2; [F] – 0.1;

reaction temperature, °C – 50; time of synthesis, hrs – 1.5; neutralization degree α – 0.9

Net polymer has gelatinization starting time (GST) equal to 10 minutes and it means that both aluminosilicate microspheres (ASM) and fullerene (F) react as process restraining agent at initial stage.

Polymeric interaction with extender surface on the one hand results in restriction of chain movement during formation of surface layer which is equivalent to the creation of additional physical network junctions. On the other hand, density reducing and therefore more loose packing of molecules should result in decrease of average number of intermolecular bonds in every volume unit.

Creation of loose packing simultaneously results in changes of intermolecular interaction within polymer because number and intensity of contacts may vary depending on molecular position one toward another. Thus, availability of boundary line may lead to augmentation of average effective number of network junctions and, as a consequence, both decrease of inturgescence and decrease of network junctions due to reducing of number of bonds polymer-polymer and, therefore, increase of absorptive capacity of material.

Figure 2 demonstrates that during increase of aluminosilicate microspheres (ASM) concentration the degree of equilibration inturgescence is changing in nonmonotonic way: firstly it reduces to the ASM concentration equal to 10 mass per cent and than it begin to increase.

Reducing of moisture adsorption of acrylate materials in comparison with uncompounded ones due to augmentation of aluminosilicate microspheres (ASM) content in composition may be explained, on the one hand, by blocking of groups responsible for inturgescence process and, on the other hand, by more defective polymeric network.

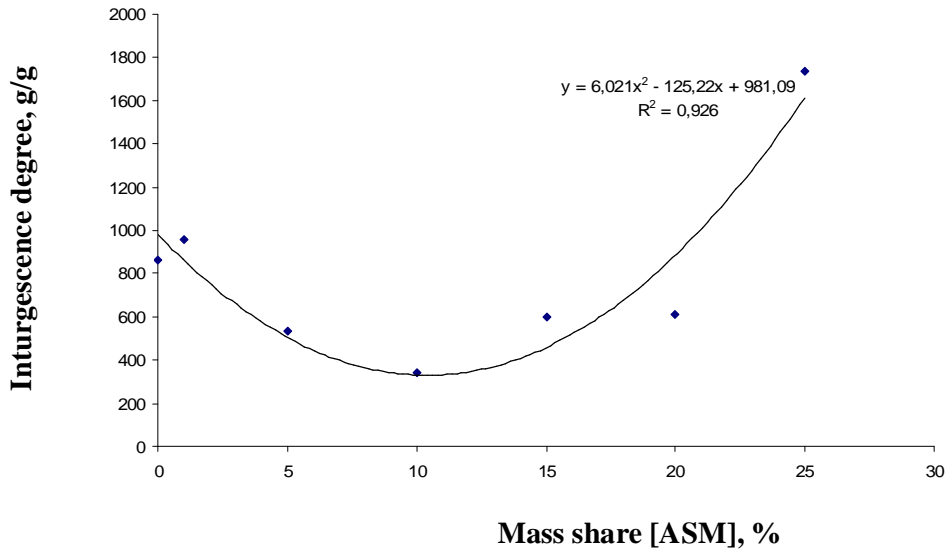


Figure 2 – Dependence of inturgescence degree of polymeric composition in distilled water under temperature of 18°C upon ASM concentration

Conditions of composition synthesis:

mass share, %: [AA] – 22; [MBAA] – 0.1; [PSA] – 2; [F] – 0.1;

reaction temperature, °C – 50; time of synthesis, hrs – 1.5; neutralization degree α – 0.9

According [10] if value of equilibration inturgescence of impregnated polymeric compositions is lower than the same factor of uncompounded ones, it is the evidence of strong interaction of polymer with extender surface, which does not violate because of affect of solvent.

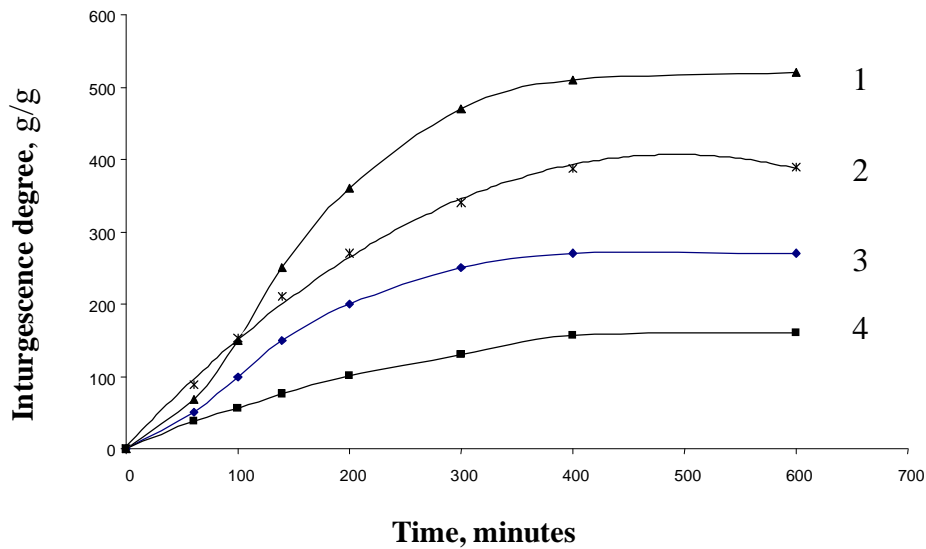


Figure 3 – Dependence of inturgescence degree of polymeric composition in distilled water under temperature of 18°C upon extenders concentration

Conditions of composition synthesis:

mass share, %: [AA] – 22; [MBAA] – 0.1; [PSA] – 2; [F] – 0.1;

reaction temperature, °C – 50; time of synthesis, hrs – 2; neutralization degree α – 0.9;

concentration of extenders in initial mixture, mass share, %

1: [ASM] – 10; [F] – 0.1;

2: [ASM] – 0; [F] – 0.1;

3: [ASM] – 0; [F] – 0;

4: [ASM] – 10; [F] – 0

Increase of inturgescence degree in conformity with growth of extender content depicts the reducing of molecular package density in case of aluminosilicate microspheres (ASM) injection into polymer.

Generally, in case of aluminosilicate microspheres (ASM) injection equal to 10 mass per cent the value of equilibration inturgescence decreases as it may be illustrated by Figure 3, while fullerene injection considerably increase inturgescence degree and you should write as follows: $Q_{\max} \leq Q_{ASF} + Q_F$.

Particles of extender – ASM – in case of its low content in polymeric matrix are the cross-links, appeared as a result of interaction of polymer with extender surface of polymeric network. Increase of extender concentration results in strengthening of material due to creation of continuous reinforcing frame as result of interaction of extender particles with each other.

Superimposition of different factors, affecting on endurance results in fragmentary extreme dependence of endurance upon degree of admission, characterized by availability of so called concentration optimum. Figure 4 illustrates the similar dependence of rupture strength of impregnated polymeric foils upon aluminosilicate microspheres (ASM) concentration as it is in our case.

Concentration optimum may be considered as the limit of inturgescence by macromolecules of absorption centers on extender surface. In case of extender content exceeding this optimum continuity of cross-linked structure is violated. According Figure 1 the materials containing 10 mass per cent of aluminosilicate microspheres (ASM) have the maximum gelatinization starting time (GST).

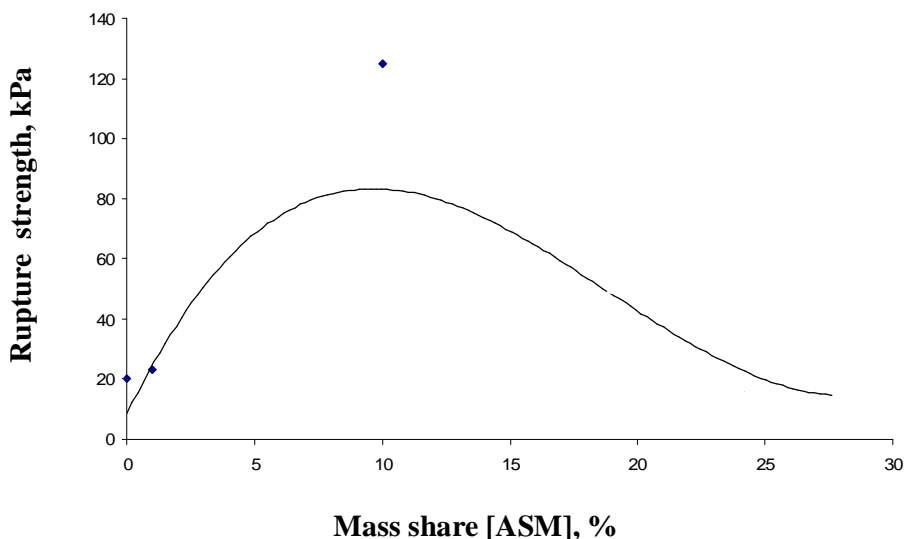


Figure 4 – Dependence of rupture strength of impregnated polymeric foils upon ASM concentration in composition

Conditions of composition synthesis:

mass share, %: [AA] – 22; [MBAA] – 0.1; [PSA] – 2; [F] – 0.1;

reaction temperature, °C – 50; time of synthesis, hrs – 1.5;

neutralization degree α – 0.9; concentration of extenders in initial mixture, mass share, %

Together with other factors material strength is defined by nature and flaw sizes, determined by tension on the top of fracture. As far as velocity of crack growth depend on degree of nonhomogeneity of materials, it is necessary to take into account influence of extender on nonhomogeneity not only from the point of view of appearance of macroheterogenicity, characterized by availability of extender particles, but by microheterogenicity as well, determined by affect of extender on structure formation.

Acrylate polymeric networks are rather defective and may have microgel structure with high level of residual stresses and therefore with low exponents of endurance and elasticity of composite materials.

Naturally, usage of aluminosilicate microspheres (ASM) reduces the value of extension coefficient depending on extender concentration and increase the quantity of sol fraction, that gives evidence of chain interruption acceleration in reaction of radical polymerization in case of extender area increase and increase of homopolymer quantity.

Combustion of binary composites

This contribution have investigated the combustibility of derived composites' samples with binary extension. The combustibility was defined in ceramic tube according national standard – GOST12.1.044-94. The results are represented in the Table 2.

Experimental data demonstrate that composite hydrogels are hardly inflammable. They consider, that during testing of hardly inflammable materials the quantity of fixed residual should exceed 80%, but it was not proved by this experiment. It is explained by high content of bound moisture in samples done, which is included into initial mass of sample.

Table 2 – Experimental data of acrylic compositions

Conditions of composition synthesis:
mass share, %: [AA] – 22; [MBAA] – 0.1; [PSA] – 2; [F] – 0.1;
synthesis temperature, °C – 50; neutralization degree α – 0.9;

No.	mass share [ASM], %	temperature of reaction chamber before injection of sample, °C	max temperature of gaseous combustion products, °C	burning time, minutes	combustion, K	mass of sample, g		weight loss of sample, %
						before test	after test	
1	5	200	181	18	0.48	41.9	22.7	45.8
2	10	200	178	17	0.36	43.7	13.9	68.2
3	15	200	175	16	0.20	37.1	10.9	70.6

Combustion of composite samples takes place in flameless mode and is characterized by extremely low propagation velocity of thermal wave.

Conclusion

Polymeric composite moisture superabsorbents, having high values of degree of equilibration inturgescence in distilled water and of other physiomechanical characteristics were derived by method of radical polymerization in aquatic medium in the presence of binary extender, fullerene and aluminosilicate microspheres. Conditions (temperature and time of process, concentration of extender and monomer, etc.) for deriving of acrylic compositions with controlled properties, viz. high level of inturgescence and endurance were defined. It was demonstrated that injection of aluminosilicate microspheres triple or quintuple values of rupture strength in comparison with uncompounded foils. Combined injection of aluminosilicate microspheres and fullerene results in synergetic effect. Derived composite materials are hardly inflammable and recommended for the furnishing of elements of fire retardant constructions.

Reference index

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