Glass microspheres in matrices of moisture superabsorbents

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Introduction

Acrylic moisture superabsorbents are widely known and usable material in many industries and farmsteads [1,2]. Meanwhile, it should be mentioned that application of acrylic hydrogels visibly limited by essential defects of materials, derived upon their basis. The most significant of them are the follows:

- high sensibility for alteration of ionic content and pH solutions (up to 2,000 g/g in distilled water, in transition to water solution of monad metal salt – up to 100 g/g depending on conditions of synthesis and storage of the sample);
- low endurance of materials and absence of possibility for manufacturing of the goods of prespecified shape;
- low speed of inturgescence.

Integration of different extenders into composition of co-polymers drastically widen potential capacities of application of acrylic moisture superabsorbents at the expense of improvement of physiochemical and mechanical properties of materials.

One of the most widely used extenders of polymeric matrix are sodium borosilicate glass microspheres (GMS), which are used in reflex compositions, lacquer coatings, etc. The possibility of such application of glass microspheres is subject to diffusion of light in different media due to difference in refractive exponents of air bell of microsphere and medium in which they are distributed. Extender is used as well for the creation of compositions applicable for external insulation of airspace equipment, laminated hydrothermoinsulation of pipe connections, fireproof garment, insulation tapes and screens for high-voltage cables, hydrothermoinsulation plates, etc.

Injection of active extenders allows to improve deformation and strength characteristics of polymeric materials, because mechanical properties of composite material depend not only on quantity of extender, but on its dispersion degree and chemical nature of extender surface.

Generally, the extender is powerful lever of regulation of operational characteristics and often is used in those cases when constructive resources of polymeric matrix are exhausted yet.

Experimental part

Consideration of results

Injection of solid dispersed extenders into polymeric matrix is performed for the purpose of alteration of physiochemical, mechanical and other properties, because one of the characteristics of active extenders is their reinforcing action. Figure 1 demonstrates physiomechanical characteristics of foils of investigated composites with dispersability less than 29 mcm. Strength dependence under magnifying of concentration of glass microspheres in the content of polymeric composition has extremely character: maximum is observed under content of 5 mass percent of sodium borosilicate glass microspheres in composition.

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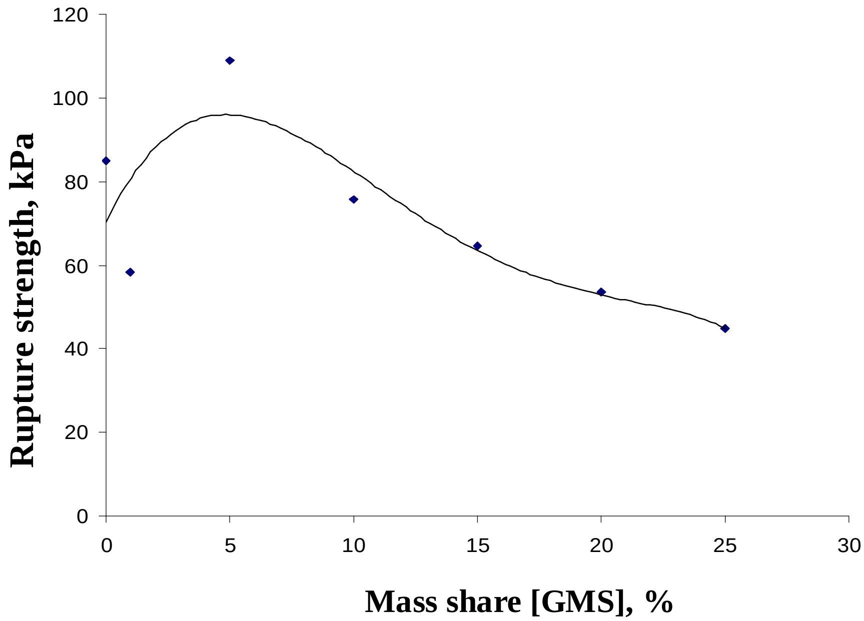

Figure 1.
Impact of extender concentration upon endurance of acrylic compositions
under moisture content ~40%

Such remarkable alterations of polymeric composition properties in the time of injection even of small quantities of extender could not be explained, if only interaction between extender surface and separate macromolecules they take into consideration without regard of participation of supramolecular structural formations, which are changing their properties under action of extender.

Extender particles, sodium borosilicate glass microspheres if they present in small quantities inside polymeric matrix are quasi cross-links of polymeric network arose as result of interaction of polymer molecules with extender surface. Augmentation of extender concentration leads to hardening of material due to creation of continuous reinforcing frame as result of interaction of extender particles with each other.

According literary data, superimposition of different factors, affecting on endurance, leads to irregular extreme dependence of endurance on extension degree, which is characterized by availability of so called concentration optimum. The similar dependence of rupture strength of impregnated polymeric foils on concentration of sodium borosilicate glass microspheres (see Figure 1) is observed as well in our case.

Concentration optimum may be considered as macromolecules' saturation limit of absorption center on extender surface. If content of extender exceeds this limit, thus continuity of network structure is violated.

The influence of different factors leading to nonmonotonic change of strength characteristics in case of extension, is the reason of transformation of extenders' reinforcing action. Effect of concentration transformation of extenders' reinforcing action appears in the form that the same extender, depending on its content in the same polymer, may weaken or strengthen this polymer.

It is possible to say about strong interaction between polymer and extender, which may lead both to improvement and degradation of endurance exponents, depending on rate of change of molecular motion of chains in surface layers.

Injection of solid dispersed extenders of different origin in polymer phase is performed for the purpose of change of physiomechanical, thermal, electrical and other characteristics of metal, but mostly the main goal is the improvement of their deformative-strength properties [5]. It is a well-known fact that generally mechanical strength of polymeric composite materials increases in proportion to content and dispersion degree of non-organic extender in composition.

In this contribution were obtained and investigated physiomechanical properties of new hygroscopic polymeric compositions based on acrylic acid (I) and N,N' – methylenebisacrylamide (II) – as crosslinking agent with binary extension. In the quality of modifying agent of polymeric matrix with binary extension sodium borosilicate glass microspheres (III) were used and fullerene C_{60} (IV), as initiating system - ammonium persulphate (V) and tetramethylethylenediamine (VI) were used.

Figures 4.5 and 4.6 evidently demonstrate that the maximum inturgescence is inherent to materials with extension equal to 10 mass percent. Polymeric materials, filled by dispersed extender, are typical heterogenetic systems with highly developed surface of phase boundary.

Interaction of polymer with extender surface leads, from the one hand, to limitation of mobility of chains during formation of surface layer, which is equivalent to the creation of additional physical cross-links of polymeric network. From the other hand, the degradation of density and, therefore, more porous package of molecules in polymer should lead to depletion of average number of intermolecular bonds per unit of volume.

The creation of unsound packing simultaneously leads to changes of intermolecular interaction in polymer, because depending on allocation of molecules one relative to another, the number and intensity of contacts between them may vary. Therefore, availability of boundary line may lead both to augmentation of average effective number of physical cross-links of networks and, as a consequence, to decrease of inturgescence, and to their degradation due to decrease of number of polymer-polymer bonds and, thus, to augmentation of absorptive capacity of material.

Figures 4.6 and 4.7 evidently demonstrate that during enhancement of extender concentration the degree of equilibration inturgescence is changed in non-monotonic way: firstly it raise up to extender concentration equal to 10 mass percent, and than it decreases. Maximum degree of inturgescence have those materials that consist of 10 mass percent of sodium borosilicate glass microspheres.

The reduction of moisture adsorption of acrylate materials in comparison with uncompounded ones along increase of content of sodium borosilicate glass microspheres in composition may be explained, from the one hand, by blocking of groups responsible for inturgescence process and, from the other hand, by more defective polymer network.

As it is evident from Figure 4.6 and Table 4.3 the maximum rate of inturgescence has the composite with mass content extender equal to 10 mass percent. The values of constants of inturgescence and of rate of inturgescence at initial sector under different extension are displayed in the Table 4.3. As it is evident from Table 4.3 inturgescence constants under extension of polymer matrix are equal to 1,5,10 and 15 mass percent. Inturgescence rate of compositions with 5 and 10 mass percent is more than of net polymer.

4.2.2 polymer composition with dispersability of extenders equal to 29-47 mcm.

Figures 4.7 and 4.8 demonstrate strength dependencies of acrylate compositions from the quantity of extender - sodium borosilicate glass microspheres. Under dispersability of extenders equal to 29 - 47 mcm the rupture strength of foils is decreased accordingly enhancement of extender in the content of polymeric matrix.

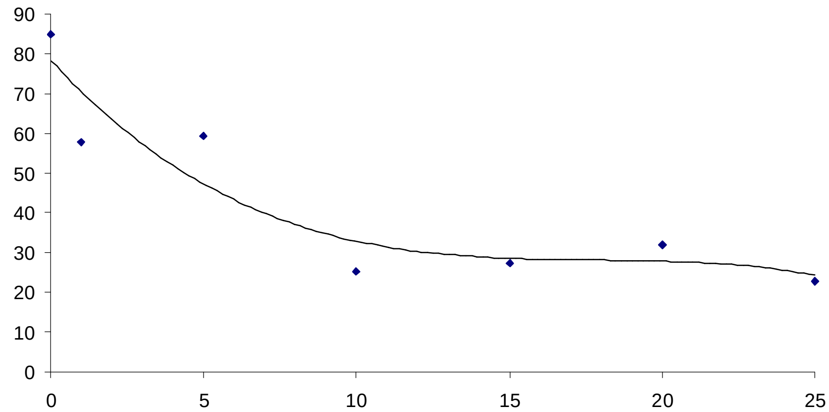

Figure 4.7
Impact of extender concentration upon endurance of acrylate compositions

Figure 4.8 evidently demonstrates that the extension coefficient of polymeric compositions with dispersability of extenders equal to 29-47 mcm have non-monotonic dependence: the materials with extension of 10,15, and 25 mass percent of sodium borosilicate glass microspheres have minimum value of extension coefficient. Figures 3.9 and 3.10 demonstrate dependencies of rate of inturgescence on process life under different concentration of extender in reaction mixture.

4.2.3 polymer composition with dispersability of extenders equal to 67-160 mcm.

Figure 4.11 evidently demonstrates the dependence of rupture strength of impregnated foils with dispersability equal to 67 - 160 mcm have the similar appearance that the appearance of impregnated foils with dispersability equal to 27 - 49 mcm

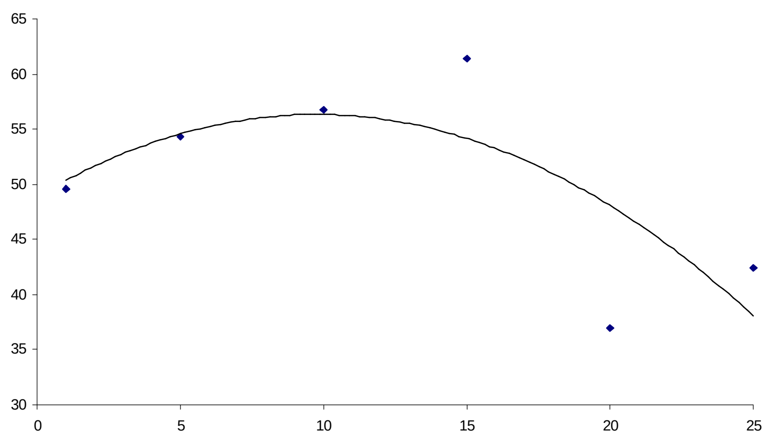

Figure 4.11
Impact of extender concentration upon endurance of acrylate compositions

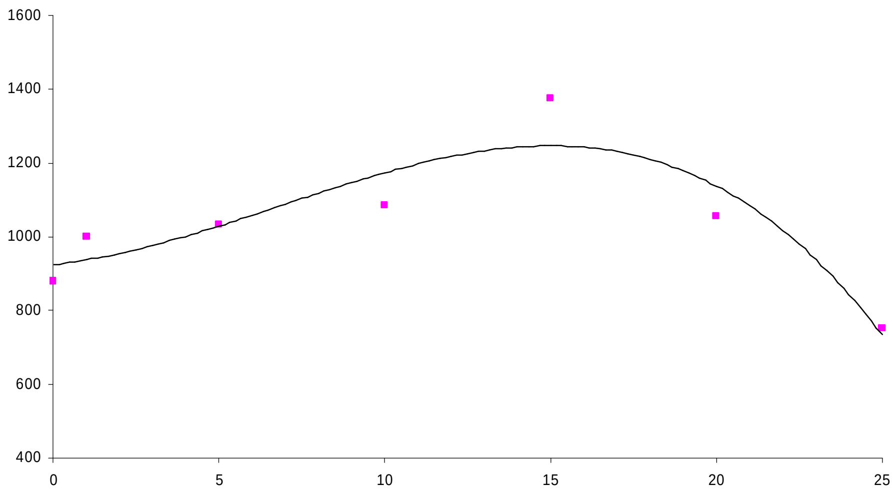

Figure 4.13
Impact of extender concentration upon maximum inturgescence of acrylate compositions

Figure 4.14 Impact of extender upon kinetics of inturgescence process depending on concentration**:** 2 – 1%; 3 – 5%; 4 – 10%; 5 – 15%; 6 – 20%; 7 – 25%.

Figure 4.13, 4.14 and Table 4.5 evidently demonstrate that the value of equilibration inturgescence degree is maximum for composites with extender concentration equal to 15 mass percent. Polymeric composition with concentration of sodium borosilicate glass microspheres equal to 25 mass percent have the value of equilibration inturgescence degree less, than of net polymer as distinct from the foils with extender dispersability equal to 27 – 49 mcm.

4.2.4 polymer composition with dispersability of extenders equal to 160-300 mcm.

Figure 4.15 demonstrates maximum rupture strength of composition with 15 mass percent of extender.

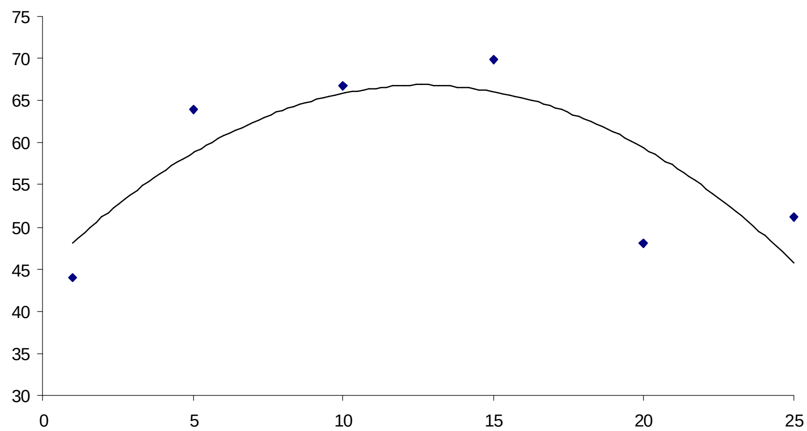

Figure 4.15
Impact of extender concentration upon endurance of acrylate compositions

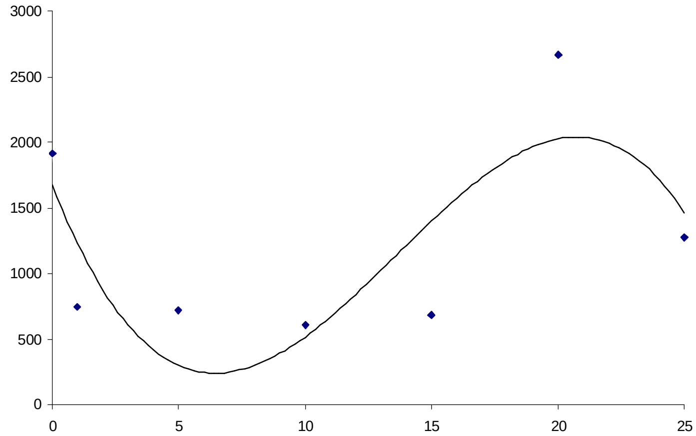

Figure 4.16
Impact of extender concentration upon extension coefficient of acrylate compositions

Figure 4.16 evidently demonstrates that extension coefficient of polymer compositions with dispersability of extenders equal to 160 - 300 mcm have non-monotonic dependence similar to the dependence relevant to dispersability of 67 - 160 mcm and 27 – 49 mcm.

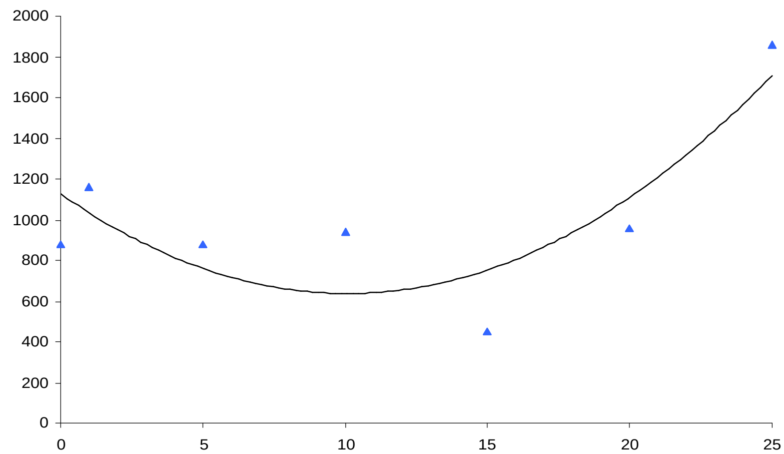

Figure 4.17
Impact of extender concentration upon maximum inturgescence of acrylate compositions

Figures 4.18, 4.10 and Table 4.6 evidently demonstrate that the value of equilibration inturgescence degree is maximum for composites with extender concentration equal to 25 mass percent. Polymeric composition with concentration of sodium borosilicate glass microspheres equal to 15 mass percent have the value of equilibration inturgescence degree less, than for net polymer. The similar dependence is incidental to compositions with dispersability of 27 – 49 mcm.

Table 4.6
The rate and constant of inturgescence of acrylate compositions
with glass extender and dispersability of 160-300 mcm.

[AF]	constant of inturgescence, minutes $^{-1}$	rate of inturgescence at initial sector dQ/dt (g/h)
1	0,0003	0,2974
5	0,0005	0,3732
10	0,0003	0,3086
15	0,0007	0,3113
20	0,0004	0,3433
25	0,0001	0,2768

4.3.1 Impact of dispersability on physiochemical properties of compositions

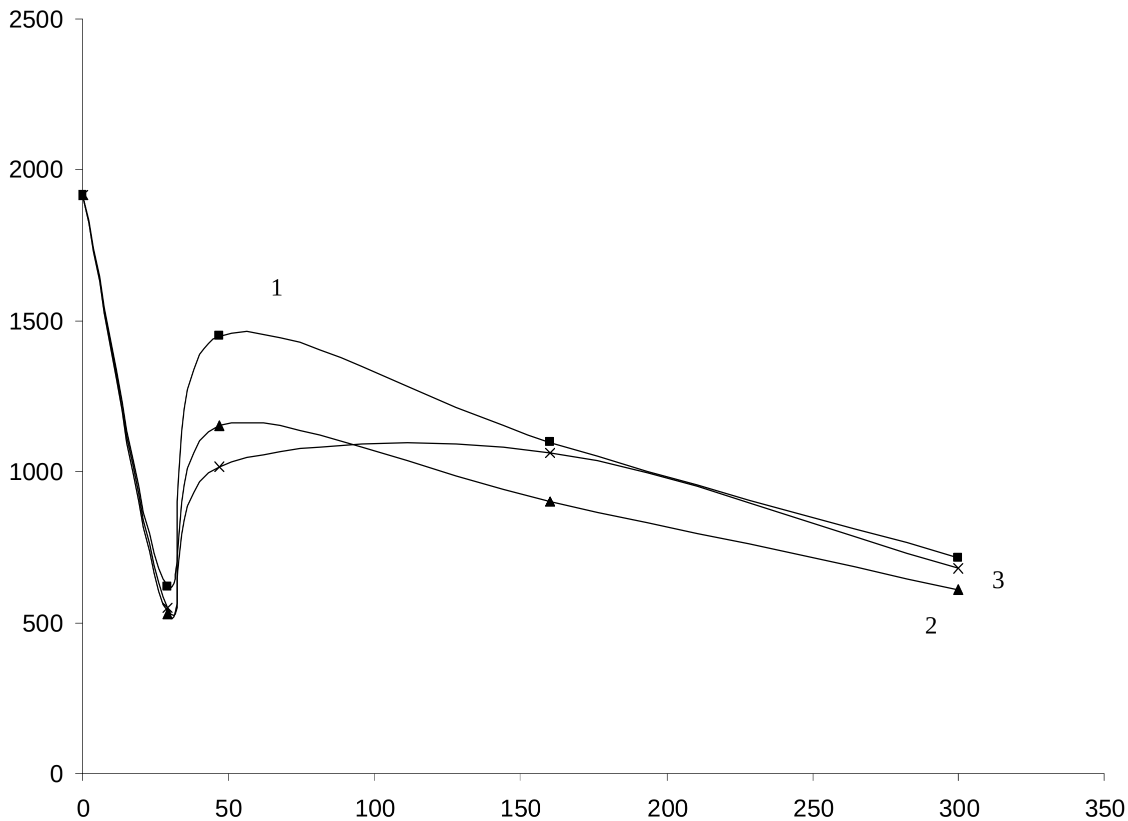

Figure 4.19 A
Impact of extender dispersability on extension coefficient of foils under different concentrations of sodium borosilicate glass microspheres: 1% – 5%, 2% – 10%, 3% – 15%

Figures 4.19A and 4,19B evidently demonstrate that the extremum is incidental to dispersability of 29 mcm and at that the minimum is incidental to extender concentrations equal to 5, 10, 15 mass percent, and maximum for concentrations of sodium borosilicate glass microspheres equal to 1, 20 and 25 mass percent.

Table 4.7
Dependence of maximum value of equilibration degree of inturgescence on concentration and dispersability of extender in acrylate matrix

	Concentration of sodium borosilicate glass microspheres					
dispersability	1	5	10	15	20	25
0	1916,66	1916,66	1916,66	1916,66	1916,66	1916,66
less, than 29	1916,66	620	530	550	2766,67	3213,3
29-47	1345	1448,3	1150	1016,5	1840	883,33
67-160	1043,33	1096,66	900	1060	1510	1040
160-300	741	716,6	607	680	2666,6	1276,66

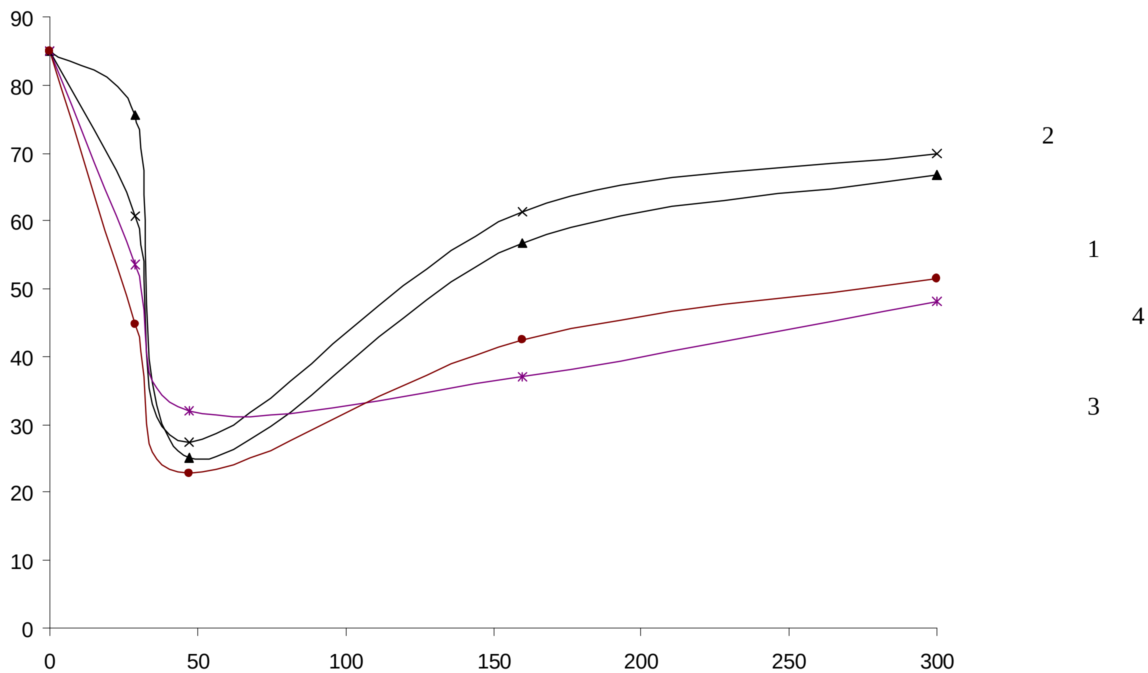

Figure 4.20
Impact of extender dispersability upon endurance of compositions under different concentrations of sodium borosilicate glass microspheres:
1 – 10%, 2 – 15%, 3 – 20%, 4-25%

Figure 4.20 demonstrates that the extremum is incidental to dispersability of 47 mcm under extender concentration equal to 10,15,20 and 25 mass percent.

Conclusions

1. Absorptive compositions were synthesized upon the basis of acrylate co-polymer with sodium borosilicate glass microspheres.
2. Acrylic compositions are characterized by high values of equilibration inturgescence degree in distilled water under concentration of crosslinking agent equal to 0,1 mass percent.
3. Impact of concentration and dispersability of extender (up to 300 mcm) on absorptive capacity of polymeric compositions was demonstrated. It was revealed that under augmentation of extender content in composition the values of equilibration inturgescence degrees and physiochemical characteristics have extreme character. Physiochemical properties of acrylic compositions with sodium borosilicate glass microspheres under different concentrations and dispersability of extender were investigated.
4. Extreme dependences of physiochemical characteristics within extender dispersability range up to 47 mcm were revealed.
5. Kinetic parameters of inturgescence of acrylate compositions modified by fullerene were investigated. Inturgescence rate acceleration under augmentation of nanocomposites in polymer matrix was demonstrated.

Reference index

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