

Polyurethane surface modification of glass microbeads

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New conditions of coating smooth surfaces of microbeads with polyurethane films has been found. This MGB having nanometer sizes are produced by hard firing of a waste building sodiumboronsilicate glass.

On the one hand polymeric coating protects glass from corrosive action of a hostile environment and on the other increases the adhesive bonds that are used as a powder fillings in a suspension environment.

This article presents the results of investigations of properties of a modified MGB and also evaluates possibilities of a new polymeric hardware application.

Introduction

In the last decade new science intensive methods of a glass waste utilization were developed. This method consists of a secondary conversion of a glass waste to the fine dispersed powder – MGB- or hollow glass micro spheres [1, 2]. The use of such a reclaim as a hardware filling allows us to enlarge an operational integrities of equipment such as strength, temperature, radiation, thermal-physic , ecological and humidity of productions and its constructions [3, 5].

Mechanical mixtures graded monolithic or hollow elements of spherical forms are characterized by storage and using safety, deficiency of blocking property and it has ability to upgrade molding properties of a filling compound in comparison with geometrically shapeless particles.

At the same time if the surfaces of microbeads don't have any local defects or surface irregularity it has lower adhesion against the coupling agent and also it can be the reason of physical-chemical deterioration of a hardened polymers. Moreover during the material maintenance there is a risk to change the material characteristics because the glass particles of a small diameter can easily to come into influence of a hostile environment.

Hence there is a need of a surface modification of a glass rolling. There is a method that allowed us to coat the surface with a thin nanosize film. Such a film is made of an adhesive active polymer that has a good reaction with the glass and at the same time a good compatible with a binding compound. Even with the min thickness this film should be fast, solid, vapourproof, with an obtainable price and manufacturability [6, 7].

Glazing coverings that is made of ultrathin surface film are widespread in different spheres of science and technology. They are formed by physical, chemical and physical-chemical processes, that are proceeded on the surface of solid matter thereby making its properties more different than properties of a substance. They are able to protect the padding from the destructive effects from the environmental hazards such as vapor of the organic liquids, acid and alkali. Also is used as a very good water-repellent insulation and reinforcing elements of a surface conditions.

Polymeric glazing of glass allowed us to regulate such factors as a level of protection from the hostile environment; light-absorption in a right spectrum range; an adhesive ability by choosing the right type of a polymer, its microstructure, branching, polarity and variation of a thickness of a coating film by changing the concentration of a polymer in a solvent, evaporation rate of a solvent, handling time and treatment temperature [8, 9].

Film coating glass is used with different purposes from making thin optical aids up to making tinted glass. However practically there is no literature on the polymeric modification of the fine-dispersed fraction of a glass.

The purpose of this work was to search formation the surface film of the sodiumborosilicate microbeads (dispersion up to 200 MCM).

Experimental part

Sodiumborosilicate microbeads of different dispersion (< 29, 46-100, < 100, 100-200 MCM) and hollow silica-alumina micro spheres of a type ACM (about 40-100 MCM) were used for modification.

Polyurethane elastomer was chosen as a film-forming substance. With stability against mechanical, temperature and physical-chemical loads it has really good adhesion to glass.

A film on the surface of glass particles was proved by different methods. Which are:

- With atomic-force microscopy
- With the metallurgical exploratory microscope MIM-10 esigned for visual observations and photographing flight-tight objects microstructure. Or this epoxy resin cylinder containing film-coating microbeads (100 MCM) was formed.
- With the use of Perkin-Elmer differential scanning calorimeter DCM 7.
- Gravimetrically. By mass increasing of a modified sample.

Glass microbeads (100- 200 MCM) and process polyurethane thermoplastic solutions with concentration of 2% were used or producing of the film coating in the last method.

In order to save the basic material from possible admixture first the MGB specimen had been heat-treated (300 °C) and then rinsing with a pure solvent and pure arrester that are used in glazing.

Both base microbeads and film-coupling glass microbeads were tested for stability against hostile environment. The analyses was made according to requirements of ??? 10134- 82 [10]. To this effect we prepared decinormal solutions of HCl and NaOH. Specimens of MGM (100-200 MCM) to within 1×10^{-4} were put into the flask and filled with 100 ml of water or acid or alkaline solutions. Flasks were held at 95 °C for 3 hours. After this every specimen of MGM quantitatively took to weighting Shott's filter with a paper membrane and then rinsed with distilled water till there would be a neutral reaction on the indicator paper. And before next weighting MGM were dried again on the filter at 95 °C till the constant mass m_1

Both base and modified (glazing) MGM and MGS were placed into latex films for determination of their role in forming the level of physical-mechanical properties of a filled polymer.

In the Table 1 there is a list of polymers of latex which differs one from another of its monomeric compositions and running abilities. In every polymer spherical glass fillings were injected in concentration of 10%, 30%, 50%. After that new films were made for definition of the ultimate strength and elongation at rupture.

Table 1– Properties of latex

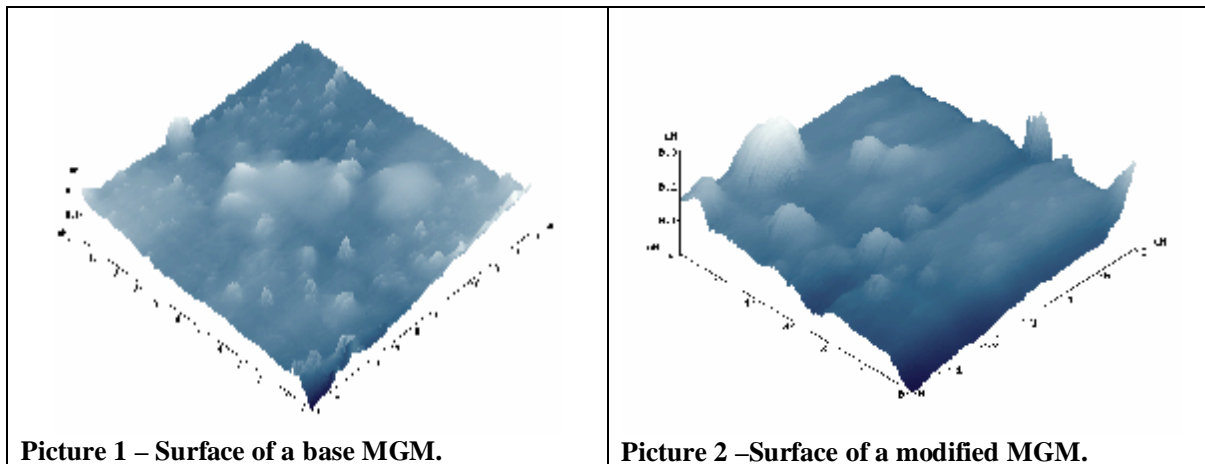
Rate	Designation		
	Latex A 5	Latex SB 278	Latex BN-2
Type of latex	Sterol-acrylic	Butadiene-styrene carboxylated	Butyl-acrylic nitrile
Mass concentration of a dry substance, %	50,1	50,0	59,0
pH	9,4	5,0	5,0
Funnel viscosity V3- 4, c	22	15	19
Min temperature of film-coating, °C	-	5	-

After film curing at 20°C for 24 hours all the test works took place on the tearing machine “Zwick” [11].

Results negotiations

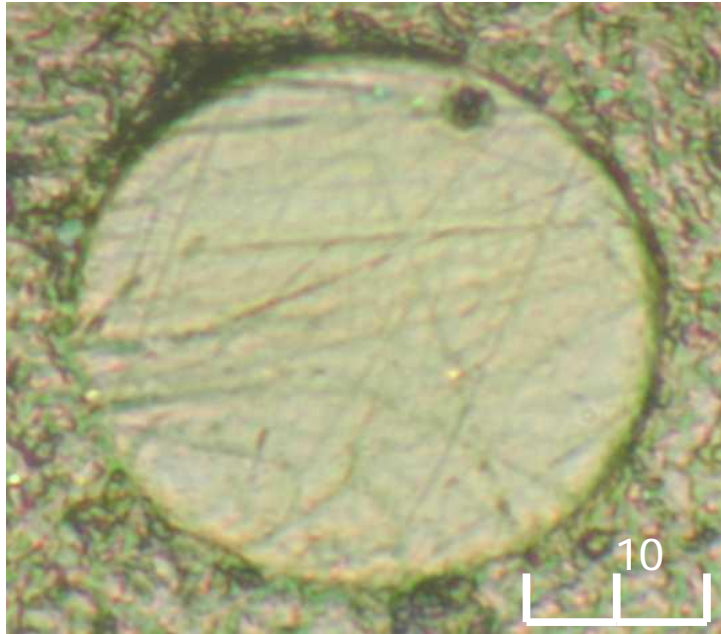
1. Sectioning

On the picture 1 and 2 there are two surfaces of a base (Picture 1) and modified (Picture 2) specimens. These pictures allow us to conclude that on the modified MGM there is a continuous film of a nanosized thickness.



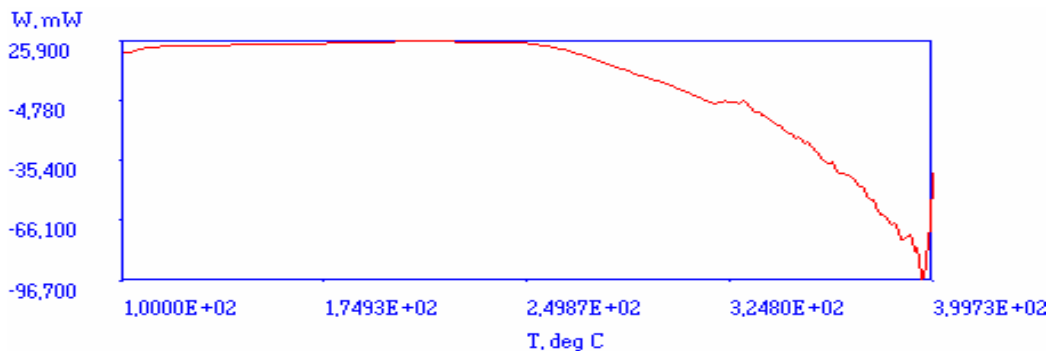
Visible diameter increase of MGM at the expense of forming the polymeric coating can be compared with the height of the defect on the surface of a glass specimen.

On the Picture 3 there is a ground surface of a section and separate MGM that is visible by microscope MIM -10.



Picture 3 – Surfaces with microbeads in a polyurethane coats (integer zooming 2000^x)

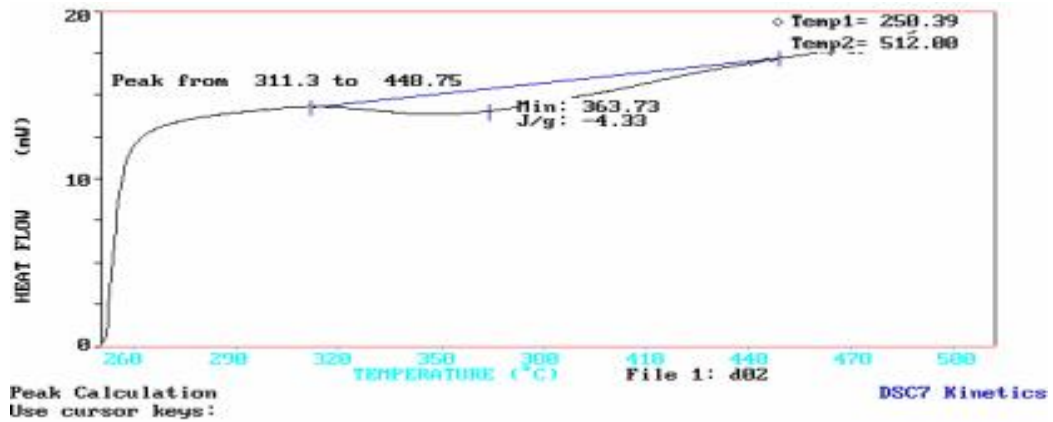
The result of measurements shows that the size of a film is much more less than the diameter of glass microbeads. And it allows us to fix an approximately thickness of a film – that is 0,02 – 0,03 mm.



Picture 4 – Decomposition curve of a glazing polyurethane.

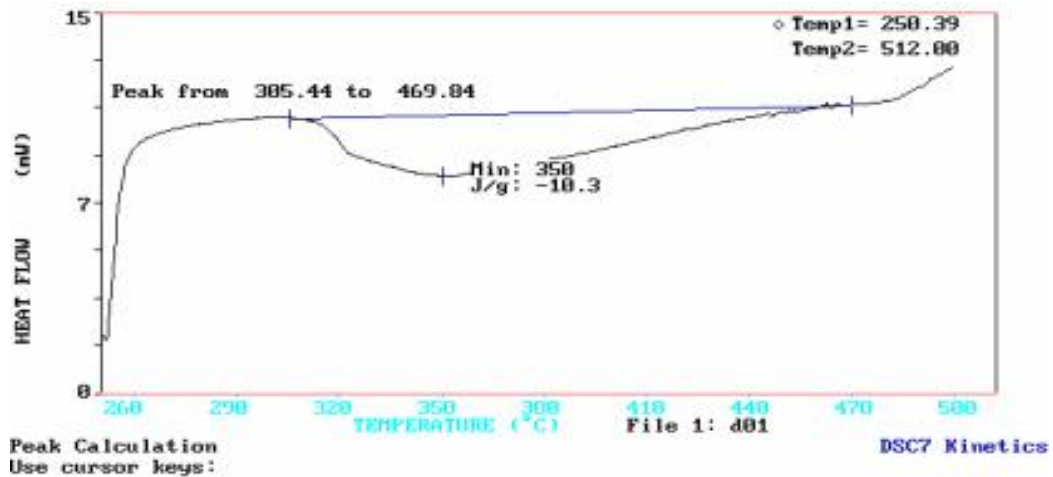
Scanning calorimeter is used for analyzing thermal characteristics of a coating film. DSK curves fix a heat current that is consumable or assignable by polymer on the surface of MGM. The rate of raising temperature was 20°C/min. Preliminary thermal decomposition of a using polymer showed the trough on the characteristic curve. This trough is equal to the exothermic effect at 400°C and also allowed us to define the temperature range of experimental procedure (250÷500°C).

Pictures 2 and 3 demonstrate curves which were obtained during researchers in the similar conditions of microbeads in the polyurethane cover that is made of process solutions of different concentrations.



Picture 5 – Heat flow curve of a film decomposition which is fell out on MGM from 2% polyurethane solution.

Comparing the heat flows of a film decomposition of different thicknesses forms on using 2% and 4% polyurethane solutions proves the fact about the difference between heat effects.



Picture 6 - Heat flow curve of a film decomposition which is fell out on MGM from 4% polyurethane solution.

Comparison between integral exothermic effects of a particular polyurethane decomposition and its covers on the MGM' surface allows us to set a cover thickness: from 2% - 0,025 mm, from 4% - 0,04 mm.

Determination thickness of a film can be made by estimating the gravity measurements. But there were one assumption that all beads in a specimen of an ideal spherical form and had the same size and the finished film would have the same thickness throughout the surface area.

According to calculation the thickness of polyurethane film fallen out from 2% polyurethane solution is 0,026 micrometers.

2. Chemical stability of modified microbeads.

It is well known that under the influence of atmospheric agents such as water, acid, alkali and etc. the glass surface begins to break down. On the first stage there is appearance of white bloom, sagging, rainbows and then blinding and cracking. That's happened because the glass contain soluble: oxide alkaline and alkaline-earth elements. The wash-out of these elements can be the reason of forming the cellular siliceous structure, silicate acid and insoluble silicates that are coagulate in a structure cell.



The process of destruction in acid, salt and alkali solutions is going quicker than in water. The reason for that is the presence of mobile hydrogen ions which play a great role in the hydrolysis.

Chemical stability of a glass, its ability to resist the destructive effect of the hostile environment are decrease while increasing of a specific surface area.

There can be a deep local destruction of a surface if soluble products don't move away from the surface.

The process of lixiviation can cause defects in a surface of a glass and the layer of silica on the surface decreases adhesive ability.

Table 2 presents the results of determination of a base and modified MGM with water, acid and alkali.

Table 2 – Decrease of mass MGM after treatment with aggressive substance .

Chemical agent	Sample	m ₀ , g (mean value)	m ₁ , g (mean value)	$(m_0 - m_1) \times 100$
				m ₀ %
H ₂ O	etalon	9,71580	9,697675	0,19
	modified	10,54590	10,53985	0,06
HCl (0,1n)	etalon	9,79650	9,75420	0,43
	modified	9,47045	9,45045	0,21
NaOH (0,1n)	etalon	8,95645	8,89670	0,78
	modified	9,75630	9,73120	0,28

Note: m₀, g – mass of a sample before experience; m₁, g – mass of a sample after experience.

Obviously that in all cases a surface modification of MGM with a thin polyurethane film influence on anticorrosive action. For example chemical stability against water increases in 3 times, against alkali in 2,5 times.

3. Properties of latex films filled with glass microbeads.

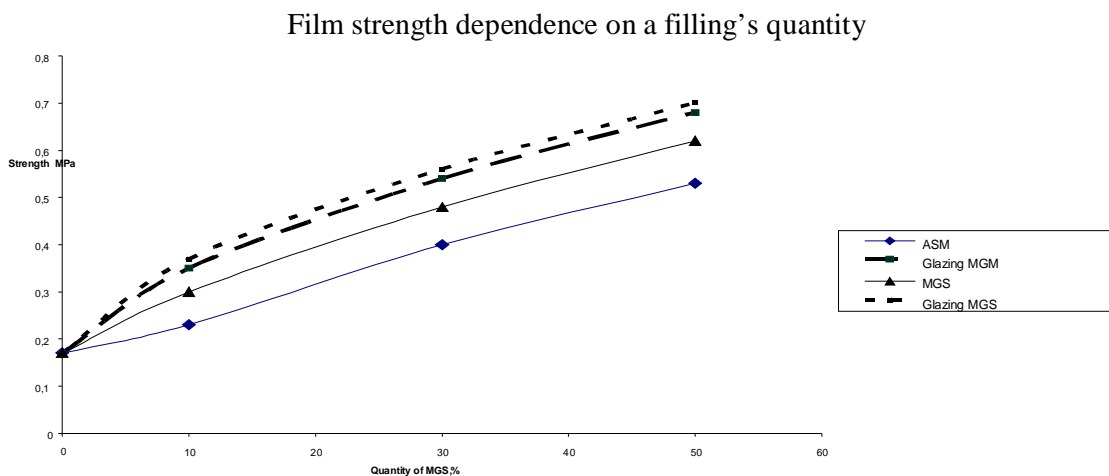
Insertion of fine-dispersed glass materials with latex compositions is a very available method of using fine-dispersed glass. Despite uniqueness properties and a big variety of latexes it is needed to be dedicated in modification concerning different technological processes [12, 14].

There are two ways of forming the composition: at the expense of high durability of a binding agent and at the expense of polymer adhesion to a filling. Both methods are worked at the same time if the increase of durability is equal to the increase of adhesion [15]. Among the binding agents the strength of composition defined by strength of the binding agent.

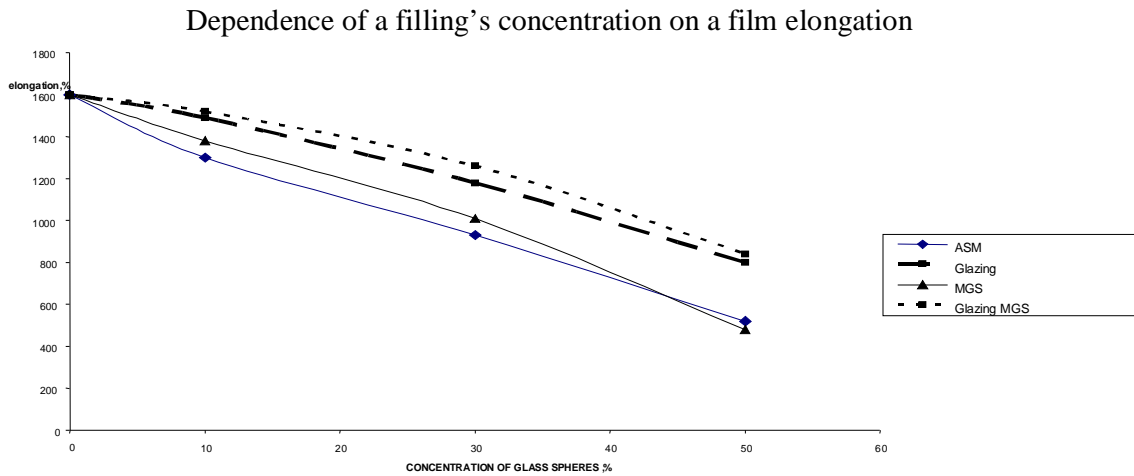
The strength of polymeric is the result of a compositions polymer's cohesion forces between macromolecules and adhesive forces that link a filling with polymer. In the issue of adhesion where the filling is placed nodes can be formed. These nodes link with each other and increase valent strength participation in a specimen's rupture. In the general case the increase of strength happens only when the work of adhesion is exceeded the work of cohesion. During the mixing each particle of a filling is covered with a polymeric film. Macromolecules of this film are orientated so that their polar groups directed to the polar groups of a filling [21].

Investigations showed that with respect to individual latex's polymer A5 the strength of a film that filled with glazing polyurethane MGS increases from 0,17 to 0,56 MPa at the minor decreasing of elongation (from 1600% to 1260%). The rupture strength of a film that is filled with glazing glass beads is bigger than the strength a not glazing MGM.

Strength and elongation of a latex film A5 dependence on a filling is showed on the pictures 7 and 8.



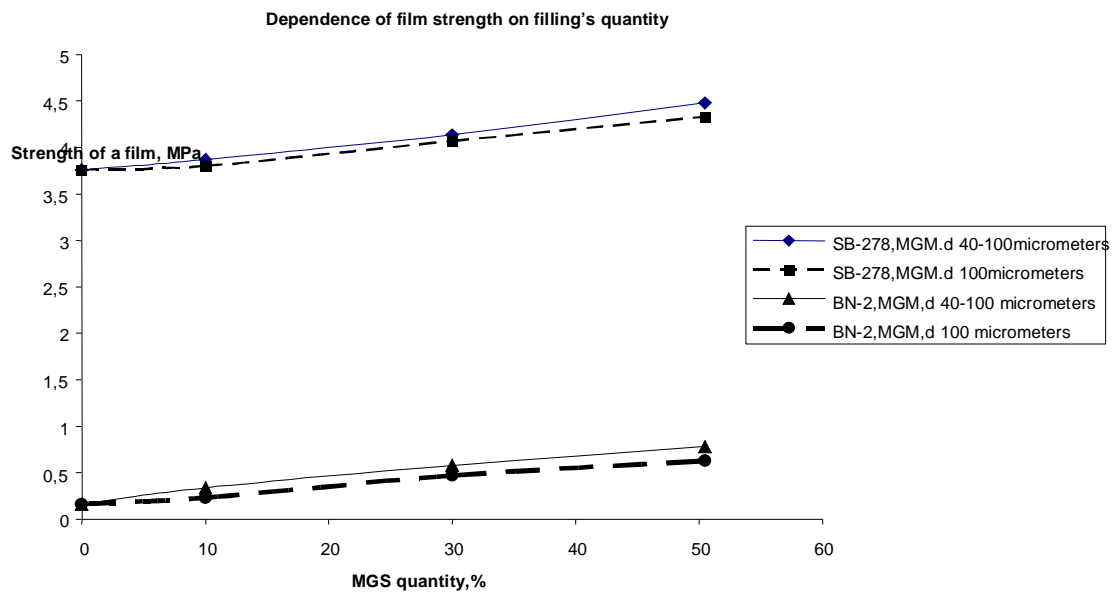
Picture 7 – Strength of latex's film A5 dependence on a type and quantity of a filling.



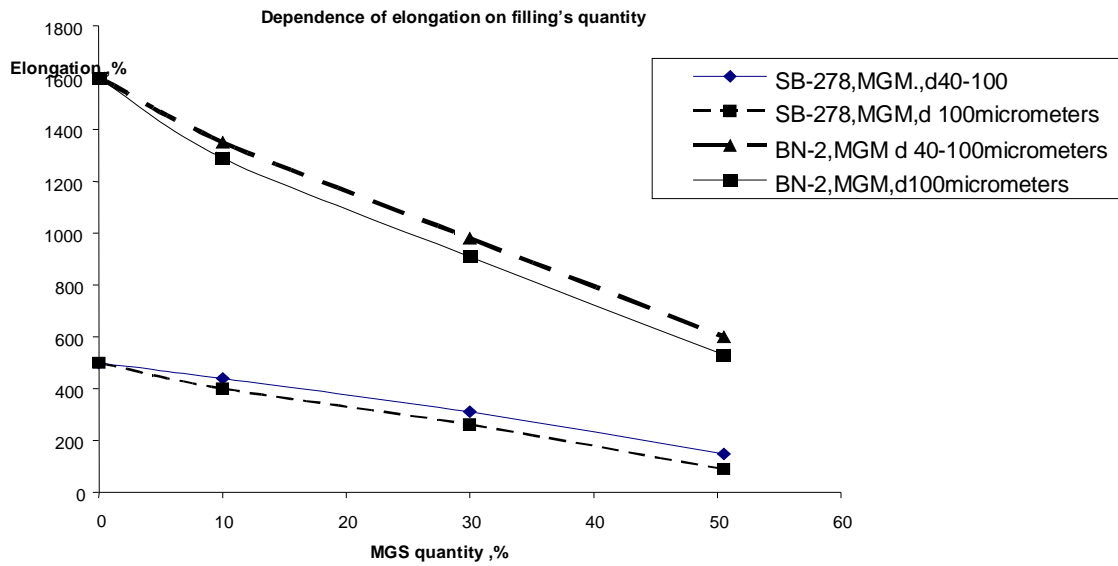
Picture 8 - Dependence of a filling's concentration on a film elongation.

With increasing of a filling in latex the rupture strength of a film is also increases (from 0,17 to 0,7 MPa in comparison with a latex film) and elongation decreases from 1600% to 480%.

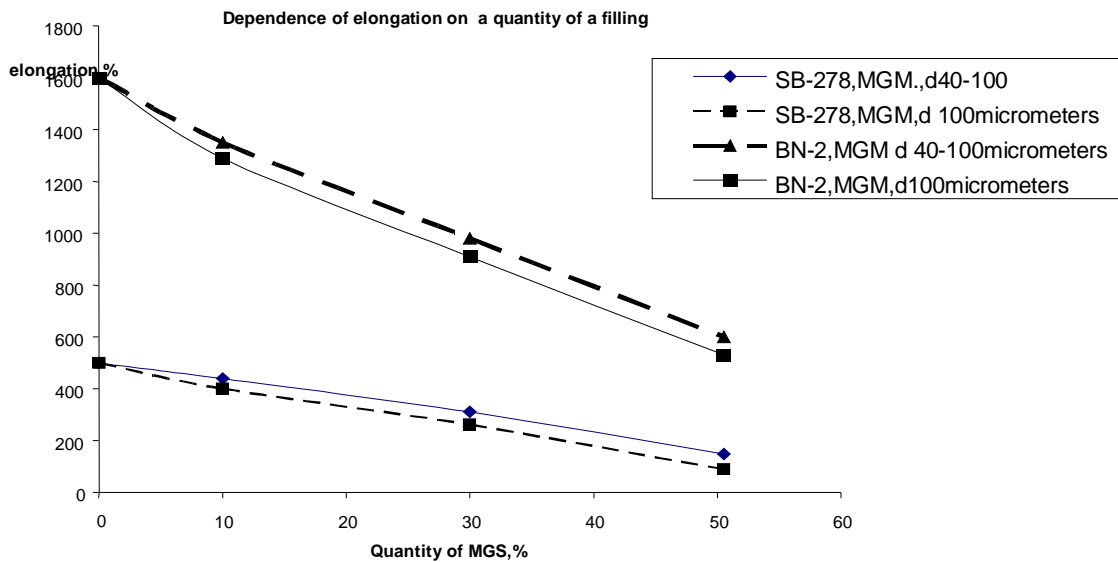
On the Pictures 9 and 10 we can see the role of concentration and of a filling dispersity at forming the level physical-mechanical characteristics.



Picture 9 – Dependence of a rupture strength of latex films SB-278 and BN-2 on concentration and dispersity of a filling.



Picture 10 – Dependence of elongation on latex films SB-278 and BN-2 on concentration and dispersion of a filling.



Picture 10 – Dependence of elongation latex films SB-278 and BN-2 on concentration and dispersion of a filling.

Filler reinforcement can be explained by “resorption” at the edges if micro cracks as a result of a stress relaxation and its redistribution of a large numbers of intergrowth cracks. Progressive crack that abut in a filling’s particle stops to grow and resume it by an additional voltage rise.

Thus increasing of mechanical strength of polymeric composition by injecting a filling is conditioned by adhesion forces and strengthening of a polymer as a result of decreasing of its thickness and orientation of macromolecules.

It is known that ideal filled polymer is a system of adsorbed thin films of a high-molecular substance that are fixed between particles of a filling and held by adhesion forces. So we can say that the strength of a polymeric composition should increase with increasing of a total area of particles that is with increasing particle's quantity and with decreasing of its sizes. But as the dispersion and quantity of a filling increase we find it more difficult to carry out a uniform distribution of a moderate-sized polymer on a wide surface of a filling. Therefore in fact the strength increases toward certain optimal limit of a filling and again after that it decreases.

From Pictures 9 and 10 we can see that the dispersion of a filling doesn't have any influence on strength's brittle and film's elongation. Physical-mechanical result of latex film when using glass spheres of a smaller diameter is much better than the use of coarse glass spheres.

Rupture strength of a film increases for the reason that boronsilicate glass spheres are very active fillings. The influence of a filling on faint latex is more stronger than on a harder latex. For example the durability strength between polymers of latex SB 278 and its composition is 3,76 and 4,48 MPa while the strength of polymers of latex A 5 and BH-2 is 0,16 – 0,78 MPa.

Conclusion

On the surface of Glass Microbeads and Hollow Glass Spheres during deposition from diluted solutions a new polyurethane film surfaces are gained. Atomic-force microscopy is a method of analyzing the surface that helped find out the evenness of a surface.

Method of differentially scanning calorimetry helps us to find out interrelation between the strength of a film and concentration of a used polyurethane solution.

With the help of microscopic, calculating and calorimetric methods was shown that the thickness of a film settled out of a solution (of 2% concentration) is 0,025 micrometers.

Surface modification of MGM of such polyurethane film protects this film from corrosion. For example chemical stability for water increases in 3 times, for acid solution in 2 times and for alkaline solution in 2,5 times.

Latex films that are filled with glass spheres have deformation-strength characteristics. Glass spheres addition increases the rupture strength of a film, but decrease its extensibility. The most optimal filling to use is 30% MSM films because specimens at higher concentration stop being elastic. Preferably to use glazing MGM as a filling because films on its base have higher strength with good elasticity. Film strength both of glazing AGM and glazing MGM is equal because of the general nature of a modified polyurethane surface.

The influence of a filling on weak latexes is bigger than on high-strength latexes.

Filling dispersion of the same nature doesn't have any influence on physical-mechanical indices of filled latex films.

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