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NANO-MODIFIED POLYMER SOLUTION FOR ADDITIVE TECHNOLOGIES

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Abstract.

By the way of particle surface organic-mineral dispersion nano modification and the acceleration of hydration process the polymer cement solution was obtained on the basis of two binders: portland cement, and polyvinyl acetate dispersion. The modification of polymeric and cement particles by a superplasticizer at the nanoscale allowed to reduce the water demand of the mixture and to obtain the required plastic strength for additive technologies. The introduction of an accelerator set at the highest possible concentration without the decrease of strength, allowed to reduce the time of the beginning and the end of setting. The strength characteristics of nano-modified polymer cement were studied. It was proved that the modification of a mixture components allows to achieve the high rates of early strength. The microstructure of polymer cement stone was studied. It was shown that the polymeric component fills the pore space and the resulting defective locations, compacting and connecting additional elements of the cement stone, which conditions the formation of a stronger and more elastic structure, the increase of fracture resistance and adhesive properties. The resulting nano-modified polymer-cement solution can be used as the printing "ink" for large-sized products without a formwork using an industrial 3D-printer.

Keywords: polymer cement, polyvinyl acetate dispersion, nano-modification, super plasticizers, additive technologies, 3D-printer.

Introduction.

One of the most modern inventions, which may soon change our world (like computers did it) are the so-called 3D-printers. Despite the fact that 3D-printing technology is a relatively new one, it can be an important tool in the architecture and construction industry. The application of 3D-printing in the world practice is designated by the term "additive technologies". Additive technology is the process of product manufacture by layered material application.

Currently, they use mainly thermoplastic polymers as the "ink" for 3D-printers. However, the use of thermoplastics is not economically viable for the industrial production of large-sized products, so scientists - developers were focused on the use of conventional mortars. After the analysis of 3D-printing technology information, we formulated the necessary physical and technological properties of the mixture, which will allow to use it as "ink":

- A certain mobility for workability;
- High plastic strength for the laying without a formwork;
- Fast adhesion for the possibility of layering;
- High adhesion between layers;
- High early strength for the accelerated construction periods.

In the free Internet space, one can find the information about the attempts of mineral construction mixes use on the basis of Portland cement as "ink". However, a mortar has a number of drawbacks: slow hardening, small plastic strength, a considerable cracking during drying, a lack of adhesion between the layers of coating, low water resistance, frost resistance [1,2]. In order to overcome these shortcomings, it was decided to create a polymer-cement solution based on two binders: mineral and organic one, and by modifying its components at the nanoscale to give it the required properties [3-7]. Taking into account the things mentioned above, the goal was set: to develop a nano-modified polymer-cement compound for the use as the "ink" to print large-size products and structures without a formwork via an industrial 3D-printer.

Methods. The determination of polymer-cement compound mobility was carried out according to the procedure developed by NIIZhB using a mini cone [8].

The determination of polymer-cement compound setting period was carried out using the device Vika (GOST 310.3-76). The determination of polymer-stone compression strength was performed using the samples of 2x2x2 cm at the age of 1, 7, 28 days. During the first 24 hours the samples were hardened in wet conditions, then the hardening took place under normal conditions.

The study of the microstructure was carried out by pictures taken by a scanning electron microscope "MIRA3 TESCAN".

Main part. The properties of the obtained polymer-cement solutions (PC-solutions) depend on many factors: cement quality, polymer type, polymer-cement ratio (P/C), water-cement ratio (W/C), and other factors.

PC materials are formed at the P/C > 0.02-0.04, when the polymer phase in a cement stone develops an organic structure unlike organic additives, such as plasticizers, administered in smaller quantities, and modifying only the structure of an inorganic component [6, 9-15]. At the values of P/C up to 0.2-0.25 hydrate phases develop crystallization-coagulation structure which is strengthened by a polymer component in the defective areas of a cement stone (pores, cracks), which conditions the formation of a stronger and more flexible structure. At a higher P/C a continuous polymer network is developed [4]. The introduction of a polymer into a mineral binder in the form of an aqueous dispersion allows to obtain the solutions with a polymer ratio up to 0.2. This is due to the fact that an insoluble polymer is in the dispersion with the form of globules of a small size (0,1..10 microns) and at the introduction in a mineral dough of more than 20% (according to dry matter) it makes an inhibitory effect on a mineral binder hardening. The main reason for the negative effect of high concentrations is water-soluble organic surface-active agents (surfactants), which are present in a dispersion at the amount from 5% to 10% from the polymer weight. The reason a surfactant addition in a dispersion is the thermodynamic instability of a system. The polymer particles in a dispersion tend to coagulate, so during the preparation of polymer-cement mixtures in order to avoid the obtaining of a material with poor properties the following must be checked: whether there is the coagulation of a polymer dispersion. The exception is the polyvinylacetate dispersion (PVA dispersion), which usually does not require an additional stabilization in polymer-cement materials. This is explained by the fact that polyvinyl alcohol is used as PVAD stabilizer, which was applied in the emulsion polymerization of vinyl acetate in PVA [5].

In order to create a polymer-cement composition for the additive technologies Portland cement A0 M500 was used with a specific surface of 408 m2/kg. The polyvinylacetate dispersion was used as a polymer binder because of a good matching with the cement compound. PVAD was administered in a percentage ratio of the cement weight to dry matter. The dispersion contains 50% of water. So if you add PVAD this water was taken into account by all means at the calculation of mixing water. During the first stage the mobility of a polymer-cement procedure was studied according to NIIZhB methods using a mini cone [8]. The water-cement ratio in each experiment was kept constant and equal to 0.375. The concentration of PVAD was calculated by dry matter to the weight of cement (Figure 1).

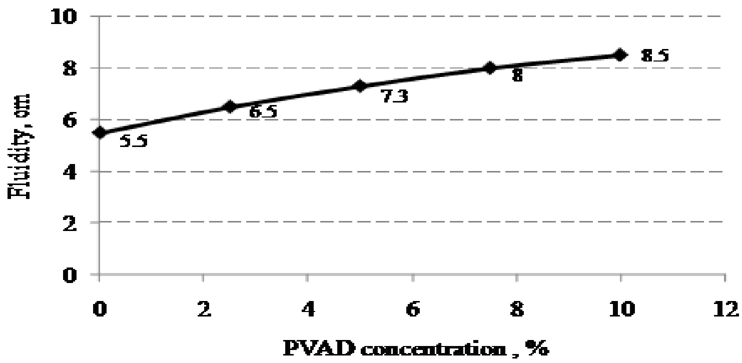

Fig. 1. The mobility of polymer-cement mixture depending on PVAD concentration.

The obtained results showed that the polymer-cement compound based on PVAD has a weakly expressed thinning effect. In our opinion, the increase of mobility is related to the fact that PVAD composition has non-adsorbed molecules based on a polyvinyl alcohol polymer. They are adsorbed on the cement particles, which brings them to peptization, and as the result, to the increase of the cement compound mobility.

Mobility and the plastic strength of the resulting polymer-solution did not meet the solution requirements for additive technologies, so it was necessary to modify the mixture. It is known [7] that superplasticizer adsorbing on the cement particles, modify the surface of phase separation at nanoscale, leading to the peptization of particles, the release of immobilized water and consequently to a system plasticizing. On the one hand superplasticizing modifiers allow to obtain highly mobile compounds, on the other hand - they have good water-reducing properties which can be used to reduce the mixing of water and the obtaining of polymer-cement mixture with a desired plastic strength for additive technologies.

In order to modify the polymer-cement mixture they used the following superplasticizers: Visco Crete 225 of Swiss company "Sika" production - this superplasticizer of a new generation of concretes and mortars based on polycarboxylates and C-3 is the domestic superplasticizer of "Polyplast" company, widely used in Russian construction industry on the basis of sulfonated naphthalene formaldehyde oligomers.

The studies showed that the imported superplasticizer Sika has an increased water reduction ability than the domestic superplasticizer C-3 (Fig. 2).

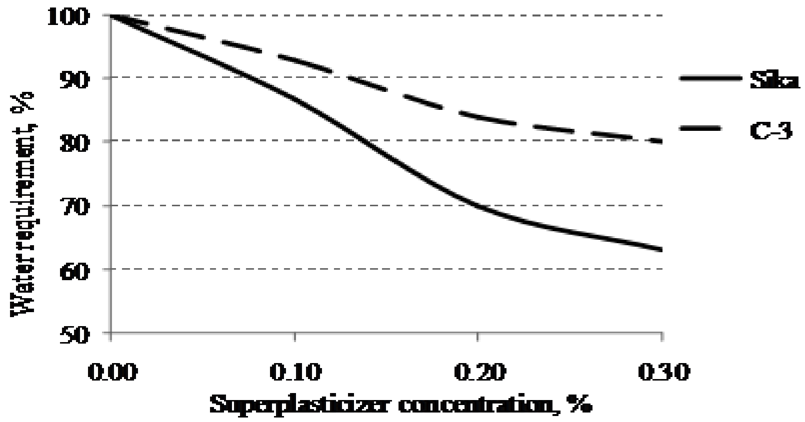

Fig. 2. The effect of superplasticizers on the water demand of the polymer compound

Thus, at the introduction of 0.3% of polycarboxylate superplasticizer one may reduce up to 37% of mixing water and C-3 at similar concentrations reduces only 20% of water. At that the mixtures of equal mobility are obtained. However, the polymer cement dough, modified at the nanoscale by a new generation superplasticizer is obtained a more plastic and workable for layering, so further studies were carried out with these superplasticizers.

Fast adhesive behavior is one of the basic properties for 3D-printing compound. It is known that the introduction of superplasticizers into a cement mixture results in the change of the setting start and end. As a rule, superplasticizers considerably increase the initial strength increase period [1]. It is not acceptable for additive technologies. Water-insoluble polymers in the form of a dispersion with the particle size of 0.1-10 microns have virtually no effect on the hydration of a binder, which allows to use a wide range of P/C (from 0.1 to 0.25). The dispersion stabilizers (water soluble surfactants) contained in the polymeric additive composition at the amount of 5-10%, or 1-2% respectively from the weight of cement, reduce hydration slightly [2,3].

The reduction of mixing water in the obtained nano-modified polymer-cement mixture allowed to neutralize the negative effect of the superplasticizer action and polyvinyl alcohol on the setting periods. However, in order to achieve the objectives it was necessary to reduce the time of the setting beginning and end significantly. Therefore, the complex of accelerators was selected in accordance with GOST 24640-91. The start and the end of modified polymer-cement setting decreased in direct proportion to the percentage increase of accelerator set. The introduction of an accelerator set at the maximum concentration without the decrease of strength, allowed to reduce the initial setting time from 135 minutes to 10 minutes, and the end of setting reduced from 210 to 20 minutes.

Fig. 3 shows the values of the average strength concerning nanomodified polymer-cement with the hardening accelerators and the cement stone control sample of 1,7 and 28 day old.

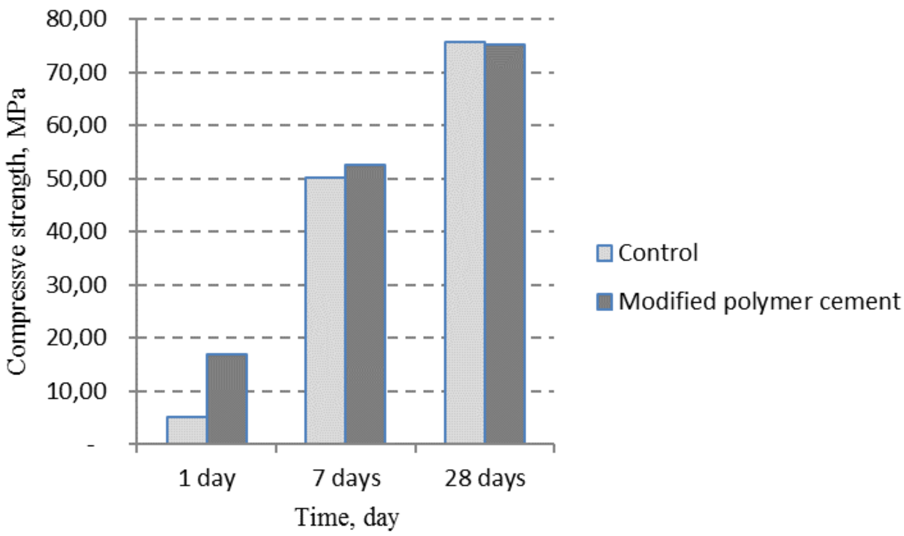

Fig. 3. Strength indicators of nanomodified polymer cement and cement stone.

The strength of one-day old modified polymer-cement exceeds the strength of an ordinary cement stone three times, which corresponds to 25 percent of 28 day old cement strength. High early strength is required for a polymer-cement solution, which will be used in 3D-printers.

In order to study the polymer-cement microstructure the images of samples were made using the electron microscope "MIRA3 TESCAN". The volumetric holes are observed in the cement stone (fig. 4), their value reaches 3 microns.

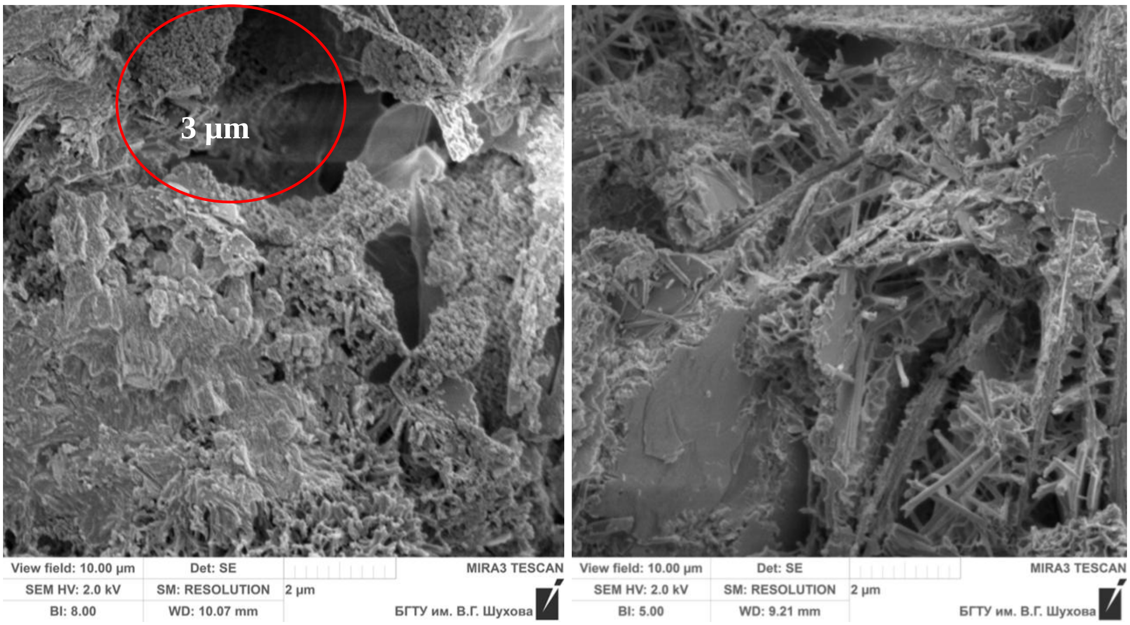

Fig. 4. The micrographs of cement and nano modified polymer cement stone.

During the period of polymer-cement hardening the mutual growing of two phases (inorganic and polymer one) takes place: polymer component fills the pore space and the resulting defective areas, sealing and connecting the cement stone structure elements additionally, which conditions the formation of a more flexible structure, the increase of adhesive properties and crack resistance. According to the obtained results you can also predict the increase of frost resistance and water resistance concerning the obtained polymer.

Conclusions. The polymer-cement composition based on two binders was obtained: portland cement and polyvinyl acetate dispersion.

They studied the water reduction ability of superplasticizers in the polymer compound. The nanomodification of polymer-cement particle surface by the superplasticizer allowed to reduce the compound water demand and to obtain the required plastic strength for additive technologies.

The influence of the obtained compound components was studied in respect of setting time. Fast adhesive behavior of nano-modified polymer-cement solution was achieved by the introduction hardening accelerator set in an optimum ratio.

The strength characteristics of nanomodified polymer cement were studied. It was proved that the modification of the particle surface concerning the components of proposed composition at the nanoscale allowed to achieve the high rates of early strength. Thus, the obtained polymer solution gains strength 3 times faster during the first day than the control solution, while the standard strength after 28 days is not less than the control sample strength.

The microstructure of a polymer-cement stone was studied. It was proved that the hydrate phases develop crystallization-coagulation structure that is strengthened by a polymer component in the defective areas of the cement stone, which causes the development of a stronger and more flexible structure.

Summary. Using the nano modification of the organic mineral dispersion particle surface, the polymer solution was obtained with a plastic strength, a high speed of setting and a high early strength. The evidence was obtained concerning the know-how "Fast setting, modified polymer-cement solution for additive technologies" [16]. Know-how relates to the field of innovative material and composite creation for additive technologies. The composition can be used as "ink" to print large-size products and designs without a 3D-printer framework.

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