Nanomodified cement composites for thin walled architectural structures

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Abstract. The article presents the studies of the processes of structure formation in the system "cement-plasticizer - crude carbon nanotubes", established the relationship with the parameters of the structure, physical-mechanical and operational properties of composite materials from the standpoint of physico-chemical mechanics of dispersed systems and shows the influence of processes on the physical-mechanical properties of cement composites. The plastic strength and physical and mechanical properties of nanomodified cement mortars and fine-grained concretes have been studied and it has been shown that the use of the developed composite materials should be used to obtain fine-grained concretes for thin-walled architectural structures.

1. Introduction

Recently, in the field of production of building materials are becoming increasingly popular nanotechnologies that provide the ability to control the processes of structure formation at the nanoscale as a result, aimed at changing the composition and structure of tumors, and hence the performance of artificial stone [1, 2].

Various technological techniques, which can be attributed to nanotechnology, allowed to significantly improve the physical and mechanical properties of various nanosized additives to modify metal, ceramic, glass matrices [3], compositions based on Portland cement [4]. The use of artificially synthesized carbon-containing nanoparticles - fullerenes, astraenes, single- and multilayer nanotubes, as additives in the composition based on Portland cement has increased strength, impact resistance, reduced deformability of artificial stone, etc. [9, 10]. The greatest increase in physical and mechanical properties was provided by carbon nanotubes [14], especially added in the form of dispersions in plasticizers [15] and at certain optimal dosages of nanotubes [16]. In [15] there was a much greater plasticizing effect from the joint use of a plasticizing additive with nanotubes than from the plasticizing additive alone. Unfortunately, the use of nano-additives in cement concrete is limited due to their high cost. Reducing the cost in this case can be achieved through the use of crude carbon nanotubes.

Investigating the reasons for the influence of nanoadditives, in particular, nanotubes, on the properties of compositions based on Portland cement [5-10], gypsum [11], various authors note their influence on the structure, hydration processes over time, the formation of distribution boundaries phase etc. Researchers [6] explain the improvement of the properties of artificial stone due to its micro reinforcement due to the creation of conditions for the formation of elongated crystalline new formation, which grow and intertwine, forming a spatial grid, reinforcing artificial stone. In [12] it was found that nanomodification of cement stone to a greater extent affects the structure of hydrosilicate phases,
increasing their density, and nanoparticles with high reactivity, large surface area and significant surface energy play the role of crystallization centers, nano reinforcement or nanofiller porosity of composites [13]. The better ability to modify slag-containing cements in [16] is also explained by the peculiarity of the morphology of new formation, in particular by the fact that in the presence of blast furnace granular slag aluminosilicates or natural aluminosilicates structures of lower basic hydrosilicates of elongated shape are formed, for which nanotubes are substrates. However, such explanations of the reasons for the improvement of the physical and mechanical properties of cement composites by nanotubes are a statement of their influence on the morphology of artificial stone and do not reveal the real mechanism of this improvement.

Although many researchers consider nanotechnology to be something new, in the technology of mineral binders and concretes, such methods and means, such as plasticizing building mixtures by adsorption of surfactant molecules, have been known since the first half of the twentieth century. In the scientific community it is believed that the hardening of mineral binders is the process of dissolving particles of matte, the formation of nanosized particles of hydrates and their aggregation into a strong stone. Therefore, it is natural to say that the scientific basis of construction nanotechnology began to create in the XIX century, V. Michaelis and A. Le Chatelier (colloid-chemical and crystal-chemical theory of hardening of Portland cement, respectively), as well as in the XVIII century. A. Lavoisier, who was the first to establish the laws of gypsum hardening [17].

However, to a qualitatively new level of nanotechnology of building materials in the middle of the twentieth century brought out the work of P.O. Rebinder, who developed colloid chemistry, outlined in its composition the physical-chemical mechanics of dispersed systems, developed on its basis a modern theory of hardening of Portland cement (hydration structure). It is the laws and methods of physical and chemical mechanics that allowed A.M. Plugin to supplement Rebinder's theory with electro heterogeneous mechanism of structure formation, to explain and make regulated water-tight permeability and excessive creep of concrete, to explain the mechanism of plasticizing action by adsorption of anionic surfactants (surfactants) on positively alluvial products permeable action on the basis of Portland cement in concrete [17].

Based on the above, the aim is to establish the mechanisms of influence of carbon nanotubes in combination with plasticizers, on the structure and properties of compositions based on Portland cement in order to obtain fine-grained concrete for thin-walled architectural structures.

2. Raw materials and test methods
Theoretical studies were performed by analyzing the compliance of the previously defined processes of structure formation and properties of Portland cement-based compositions with carbon nanotube additives and plasticizing additives to the known laws of colloid chemistry and physical-chemical mechanics of dispersed systems.

Portland cement CEMII/A-S-32.5, plasticizing additives such as: lignosulfonate with esters of polycarboxylate (SikaPlast 520), naphthalene formaldehyde, melamine formaldehyde (Muraplast FK-98), polycarboxylate were used for experimental researches. As a nanoadditive, crude multilayer carbon nanotubes coated with a silicon airgel with interplanar distances of 0.34–0.36 nm and a particle size of 60-200 nm were used.

Aqueous dispersions were made from carbon nanotubes and plasticizers using a cavitation mixer, in which the content of nanotubes and plasticizers was taken as 1% by weight of cement.

Determination of the features of the structure of artificial stone and identification of its elements was carried out by physical-chemical methods using a scanning electron microscope REMMA-102-02.

Physical-mechanical and operational properties of cement compositions and fine-grained concrete were determined in accordance with current regulations.

3. Results and discussion
Comparison of electron micrographs of treated (CNT) and untreated carbon nanotubes (UCNT) (Fig. 1) and studies of crude tubes showed that the diameter of the tubes is 10–20 nm, and crude tubes contain a significant number of gel formations (Fig. 1, b), which consist of an aerosil residue in the amount of 6–20% and graphite in dimensions comparable to the transverse dimensions of nanotubes of 10–20 nm.
Figure 1. Electronic micrographs of carbon nanotubes:
a - treated, transmission electron microscope; b - untreated, scanning electron microscope, x2500

General view of the model center and layout of thermocouples: 1 - container; 2 - supports; 3 - a stack for burning stack; 4 - thermocouples.

As shown in [15], in the case of modification of cement systems by nanotubes, the largest increase in physical and mechanical properties provided their introduction in the form of dispersions in solutions of plasticizers [15]. Plasticizing additives in cement concretes are anionic surfactants, the molecules of which are diphilic and consist of a hydrophobic hydrocarbon radical R and hydrophilic functional groups, which dissociate in aqueous solution, resulting in the formation of macroanions $R-(SO_3^-)_n$ or in polycarboxylate $R-(COO^-)_n$ (Figs. 2, 3, a). Carbon nanotubes (Fig. 1, 3, b) are hydrophobic, so they do not acquire a surface charge in the aqueous medium. In an aqueous solution, according to the rule of polarity alignment, surfactant molecules are adsorbed on the surfaces of nanotubes by their hydrophobic parts, forming nanoparticles that have a negative surface charge (Fig. 3, c). In areas of the surface of nanotubes covered with amorphous silica, the adsorption of surfactants does not occur.

Figure 2. Molecular structure of surfactants used as plasticizers, lignosulfonate (a), naphthalene formaldehyde (b), melamine formaldehyde (c) and polycarboxylate (d) type.
The fractional composition and average size of these particles, as well as the stability of dispersions of them in a surfactant solution of lignosulfonate with polycarboxylate esters, naphthalene formaldehyde, melamine formaldehyde, polycarboxylate type were studied. It was found that the particle sizes of dispersions are for surfactants of the type: lignosulfonate with polycarboxylate esters, melamine-formaldehyde - 5–1000 nm, on average 200 nm; naphthalene-formaldehyde, polycarboxylate - 30–1500 nm, on average 300 nm. The minimum average particle size was observed for the content of nanotubes in the dispersion of 0.5–1%, which obviously provides the limiting monomolecular adsorption of surfactants on their surface. The obtained dispersions are stable over time, sedimentation and aggregation of nanoparticles were not observed.

It is known that the high shear resistance and viscosity of cement paste, mortar and concrete mixture without plasticizer additives due to the fact that on the surface of Portland cement particles in the aqueous medium are formed areas with negative surface charge (C₃S, C₂S), which predominate and with positive surface charge (C₃A, C₄AF) [18–20]. After mixing with water between oppositely charged areas, electrostatic attraction forces appear, which together with the always adhering molecular forces cause high shear resistance and viscosity of the entire dispersed system (Fig. 4, a).

The mechanism of action of plasticizing additives is the adsorption of anionic surfactants on positively charged areas of the surface of Portland cement particles C₃A, C₄AF (Fig. 4, b). Due to this adsorption, depending on the number of anionic functional groups, neutralization or even recharging of
C₃A and C₄AF regions occurs, which eliminates electrostatic attraction from interparticle interactions, significantly reducing the shear resistance and viscosity of the system.

Nanoparticles - surfactant aggregates with carbon nanotubes have a significant number of anionic groups oriented in all directions along the tube (Fig. 3, c). Adsorbed on sites C₃A, C₄AF, they do not neutralize their positive surface charge, but recharge it to an intense negative, causing growth in the interparticle interactions of the repulsive component. This causes a greater plasticizing effect of the combination of surfactants with carbon nanotubes than from surfactants alone.

Based on this structure of nanoparticles - surfactant units with nanotubes, their surface charge is negative both in areas with adsorbed surfactant molecules and in areas covered with amorphous silica. Therefore, they can be substrates for crystal hydrates that have a positive surface charge - portlandite Ca(OH)₂, hydroaluminates and hydrosulfoaluminates of calcium.

Experimental verification (Fig. 5) of the proposed mechanism of plasticizing and structure-forming action of nanoparticles - surfactant aggregates with carbon nanotubes showed that the greatest effect on reducing the shear resistance and viscosity of cement paste over time is observed in the use of plasticizing additives lignosulfonate with polystyrene esters or melamine-formaldehyde (Muraplast FK-98) type and UCNT in the amount of 0.05% [11,12]. It was found, that the presence of a plasticizer in slag-containing cement paste significantly reduces its plastic strength and prolongs the induction period, with the greatest elongation (about 3 hours) occurs with the introduction of additives polycarboxylate type MC Power Flow 3100 and lignosulfonate with polycarboxylate esters.

![Figure 5](image_url)

**Figure 5.** Change in plastic strength over time of compositions based on slag-containing cement (1), with the addition of plasticizer (2) and modified dispersions containing nanoadditives (3) in plasticizers of different types: a) PC (Power Flow 3100), b) NF (CII-1), c) LST + EP (Sika-Plast-520), d) MF (Muraplast FK-98): 1 wt.% UCNT.

The study of the influence of the structure-forming action of nanoparticles - surfactant aggregates with carbon nanotubes showed that the greatest effect on increasing the strength of artificial stone is observed in the case of plasticizing additives lignosulfonate with polycarboxylate esters (SikaPlast-520) or melamine formaldehyde (Muraplast FK-98) 05%. The compressive strength of slag-containing cement stone due to the introduction of nanoscale additive increased by 21–39% (Fig. 6, a) bending strength - by 13–24% (Fig. 6, b).
Figure 6. Kinetics of change in strength for 28 days of hardening under compression (a) and bending (b) of samples of slag-containing cement mortar modified by dispersions of nanotubes in plasticizers of different types with different content of nanotubes

In addition, the positive effect of nanomodification on the pore structure of the cement matrix in the direction of formation of micro- and nanopores of close diameter has been established, and their ordering is also observed. It is shown that the structure is dominated by closed pores, which increases the water resistance and corrosion resistance of the composite material. The effect can be explained in terms of the energy interaction between the components of the system, as carbon nanoobjects create a large number of uncompensated surface charges, and the formation of electrokinetic barriers to the transfer of aggressive substances through the body of artificial stone.

The introduction of UCNT dispersions leads to structural changes in the cement-sand mortar with the formation of a dense shell on the surface of the solid phases of cement grains and quartz sand. The number of contact interactions in the structured boundary layers increases and spatial frame cells are formed in the cement matrix with dense layers of crystal hydrates, which leads to a general compaction of the matrix.

The study of the microstructure of nanomodified artificial stone shows that there is the formation of lamellar calcium hydrosilicates of hexagonal shape, which increase in layers, forming a fairly dense and impermeable structure (Fig. 7). Such new formation in the hydration products of the sample with a pure plasticizer are completely absent. Over time, the presence of nanotubes contributes to the complete recrystallization of needle crystals into plates, which are located on top of each other and in shape resemble a crystal lattice of graphite. This phenomenon can be explained by the epitaxial growth of calcium hydrosilicates due to the formation of crystals on the surface of carbon nanotubes, which are formed from several rolled into a tube hexagonal graphite planes.
It is confirmed that the composition of the cement matrix plays a decisive role in the composite's acquisition of special properties, and the combination of slag-containing cement with bentonite in the presence of NVNT in melamine-formaldehyde plasticizer gives the best results for all studied performance properties. Cement composites are obtained, which are characterized by compressive strength of 35...49 MPa, flexural strength of 12...17 MPa, water absorption coefficient of 0.018...0.021 kg/m²√h, water resistance of 0.74...0.87 MPa, corrosion resistance in sulfate medium 0, 73... 0.92, frost resistance up to 200 cycles. Studies have also shown high crack resistance of nanomodified cement composites, which is 1.5...1.7 times higher than similar to the unmodified system.

A composite material has been obtained, which can be used as a cement matrix in the creation of fine-grained and coarse-grained concrete, special-purpose solutions, including waterproofing, repair, protective coatings for the restoration of reinforced concrete structures.

The most effective use of nanomodified cement composite material is planned as a matrix for obtaining fine-grained concrete for thin-walled architectural structures for landscape design, working under the influence of dynamic loads and aggressive influences of water and sulfate environments, elements of enclosing structures river banks, etc.

4. Conclusion
1. It is established, that for the modification of composite materials based on Portland cement in order to improve their physical and mechanical characteristics, it is advisable to use as an additive an aqueous dispersion of crude carbon nanotubes and anionic surfactants - plasticizers for concrete. Part of the surface of nanotubes is covered with amorphous silica, the rest is a hydrophobic carbon surface.

2. In an aqueous dispersion, carbon nanotubes and molecules of anionic surfactants form nanoparticles-aggregates with a negative surface charge, in which according to the rule of polarity alignment surfactant molecules are adsorbed by hydrophobic hydrocarbon radicals on carbon surfaces of nanotubes, hydrophilic anionic functional groups - outward in all directions.

3. The plasticizing effect of co-administered anionic surfactants and carbon nanotubes is greater than the plasticizing effect of surfactants. This increase is due to complete recharging of positively charged parts of the surface of Portland cement particles due to adsorption of these nanoparticles-aggregates instead of neutralization due to adsorption of surfactants only and complete replacement in contacts.
between cement particles in the test of electrostatic attraction between oppositely charged areas of electrostatic surfaces.

4. Nanoparticles-aggregates of surfactants and nanotubes cause a structuring effect on cement stone, playing the role of negatively charged substrates for crystal hydrates of portlandite and calcium hydroxysilicates with a positive surface charge. Together they form in the cement matrix a reinforcing spatial frame structure with dense layers of crystal hydrates, which causes its overall compaction and strengthening. Amorphous silica contained in crude nanotubes is involved in the hydration of Portland cement with the formation of additional low-base calcium hydroxysilicates with a negative surface charge, which build up in layers on lamellar calcium hydroxysilicates and form a fairly dense and impermeable structure of cement.

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