

Prospects for the Development of Nanostructured Polymer Composites in the Chechen Republic

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ABSTRACT

This work presents the analytical form of determination of polymer composites market. It was noted that saturation with these materials in regional dimension (exemplified by the Chechen Republic) is large enough, and along with the growing construction market this need is institutional. It was determined that the lead issue remains to be the high percentage of borrows in the development industry and the lack of specialists on nanomaterials. The prospects of development of nanostructured building polymer composites on the base of scientific institutions in the Chechen Republic were analyzed. The status of the issue was studied and the basic directions of scientific researches in the field of nanomaterials science were identified. It was found that the solution to the problem of building nanocomposites development, including nanostructured polymer composites, would provide creation of new products, semi-finished products, designs and details of buildings and structures, efficient technologies of their erection, and conditions for comfortable and safe life. Authors encourage in the article to undertake the development of materials under the study and gradually shift to filling the composite materials from local components at the expense of attracted private investments. Such strategy should give results within 10-15 years. The possibility of using foreign experience is predicted. Not only existing technologies were analysed, but also the trend lines in the leading western systems and commercial development companies.

KEYWORDS Nanotechnology, polymer composites, autoclave, high pressure, quasinanoparticles, nanoparticles, development, structural analysis, materials science. ARTICLE HISTORY Received 2 September 2016 Revised 29 November 2016 Accepted 11 December 2016

Introduction

Nanotechnology is one of the newest directions in science and engineering, which becomes the main element of a competitive industry, especially if appropriate conditions are developed for the rapid introduction of nanotechnologies with a view to creating high-quality market of new products and services (Arduini et al., 2016). Nanotechnology is one of the key directions in the development of industry and

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scientific and technical progress of society (Zhou et al., 2016). Their development is the way to managed synthesis of molecular structures intended to ensure the acquisition of objects not from conventional raw material resources but directly from atoms and molecules (Lupu et al., 2016). Experts estimate that nanotechnology has become the most important direction of the technological development of the world's leading powers of the twenty-first century (Petrarca et al., 2017) Being an institutionalized national priorities, these innovative technologies provide the overall impetus for the development of other industries (Menshutina, 2006; Kuladzhi et al., 2015). In our opinion, the Chechen Republic has all the necessary conditions for the development of nanotechnology (Matias et al., 2016).

In the Russian Federation, synthesis and study of new substances, and development of materials and nanomaterials (including composites and nanostructured polymer composites with predefined properties and functions) are among the main directions of fundamental researches in materials science operated by the FASO of Russia and the Russian Academy of Architecture and Construction Sciences.

In terms of synthesis and study of new building materials with given properties and functions the most promising are polymer composites (Mohiuddin& Tung, 2016). Polymer composites are building concrete and mortar, which pores are filled with polymers (Strokova et al., 2013). Typically polymer composites are obtained by imbuing the composite with monomer with its subsequent polymerization directly in the pores of a composite (Wu et al., 2016). As a result of composite structure seal by polymer and effects of several physico-chemical factors, its durability increases multiply, frost resistance and resistance in aggressive environments increases significantly, other properties improve as well. Composites of various types and compounds may undergo treatment; different substances, compositions and technologies may be used for filling-in composite pores (Huang & Wang, 2016). Products can be processed on all depth through, by separate areas or only from the surface. Due to the wide variety of possible solutions, great prospects for material management, improvement of building constructions, product properties manufacturing technologies and construction production are given (Akimov & Prezhdo, 2016).

Further treatment of a composite by polymers allows obtaining more solid and durable materials and products, reduce their weight and material intensity, economize metal and binder, extend the scope of concrete and ferro-concrete products usage, efficiently use local materials, mixed binders, secondary industry products, chemical additives in their production, get materials and products with new properties, such as long-lasting decorative, electrotechnical, super wear-resistant, impermeable, corrosion-resistant products, develop new designs and products, improve the effectiveness of the technology of concrete and ferro-concrete products in some instances, improve their installation and assembly, successfully apply adhesion of products, undertake repairs and reinforce the existing concrete and ferro-concrete structures (Lee & Stokes, 2016).

Development of technology, studying the structure and properties and definition of rational application field of nanostructured polymer composites traditionally called "polymer concrete" was started back in the Soviet Union and other countries since the mid-sixties, although some attempts to seal the structure by other materials, for example, bitumen or fluosilicate, were known earlier (Bazhenov, 1983; Murtazaiev et al., 2015a, 2015b). Application for treatment of concrete and mortars of special

monomer- and polymer-based compositions and the use of special technology allowed making decisive progress in this direction.

The realization of nanotech direction of fundamental research in construction sphere, which is very important in the context of the Chechen Republic, may bring the development of polymer composites on special binders, including nanocomponents. Technology of such composites will be implemented on the theoretical base of obtaining artificial conglomerates, which define great opportunities of improvement the structure and properties of nanomaterials by using complex modifiers, including various chemical additives (surfactants), microsilica, nanosilicates and special technologies (Bazhenov & Mazhiev, 2011; Bataev et al., 2007; 2008; 2012; Mazhiev & Betilgiriev, 2012).

In the foreseeable future the development of nanostructured polymer composites technology is predicted to go in the direction of nanocomponents and special technologies of preparation, care and hardening (Eastlake et al., 2016; Jagiello et al., 2016; Xue, 2016).

Material and methods

Major attention should be given to the development of special modified additives and purposeful development of molecular structure of chemical additives (Bazhenov, 1983). Polymer composites under the development should be multicomponent.

The use of special technologies (high pressure, temperature, low discharging, the use of complex modified additives and modifiers, and other methods of intensification) allows getting nanocomposites with given physical mechanical properties (Bataev et al., 2007). Adding various discrete phases to nanocomposite compositions allows getting various structural, structural insulating, cellular heat-shielding, decorative, conductive, dispersion reinforced, radioactive shielding and other special types of materials (fig. 10).

Introduction of complex modifier including surfactants, fine mineral component, quasinanoparticles and substances regulating their own material deformations, improves the properties of nanostructural polymer composite.

The nature of action of surfactants on the composite mixture is determined by the structure of surfactant molecules and the ratio of its hydrophilic and hydrophobic parts.

The mechanism of action of surfactants, which provide significant increase of the mobility of composite mixtures is mainly in reducing the amount of water for moisturizing solid particles due to reduction of water surface tension, coefficient of internal friction and in smoothing the microrelief of hydratable binder grains, as well as in the occurrence of negative electrokinetic potential, which contributes to deflocculation and dispersion of particles and colloidal nano-sized new formations.

Performed research work established that the issue of the development of address modifiers, including surfactants, nanoparticles and quasinanoparticles remains unresolved.

The specified problem can be solved in the following directions:

- development of theoretical basis of creation of complex modifiers, nanoparticles and quasinanoparticles;
- the study of chemical and physico-chemical properties of surfactants for their targeted use;
- the study of physical, physico-mechanical and physico-chemical properties of nanoparticles and quasinanoparticles;

development of usage technologies of targeted modifiers, nanoparticles and quasinanoparticles.

Results and discussion

Currently the studies on development of nanomaterials and composites, a polymer composites have started in the Chechen Republic (Bataev et al., 2008). The researches deal with the studies of dynamic patterns of physico-mechanical properties of building polymer composites towards the reduction of the active and inert fillers size from 10^{-2} m to 10^{-9} m. It should be noted though that changes of physico-mechanical properties of building polymer composites within the range of inert fillers diameters from 10^{-2} m to 10^{-4} m are highly researched. Researches are performed at ultrahigh pressures and discharges.

To achieve the stated objectives in the scientific areas autoclave was restored and put into operation (Figure 1). Autoclave hydraulic pressure test was under the pressure of 2100 kg/cm², and operation is permitted under the pressure not higher than 1650 kg/cm². Excess pressure of 1800 kg/cm², working environment of autoclave camera is spindle oil. Temperature change interval is up to 400°C. Autoclave conceptual model is shown in Figure 2.



Figure 1. High-pressure autoclave

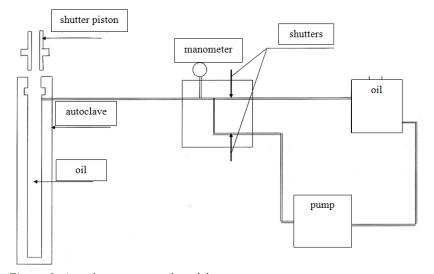


Figure 2. Autoclave conceptual model

Testing and calibration stand of ultrahigh-pressure measuring equipment (Figure 3), which allows not only holding calibration works, but also obtaining high pressures (up to 3000 bar) manually had passed commissioning and entered into service.



Figure 3. Testing and calibration stand

The vacuum station (Figure 4), which allows applying quasinanofilms to the surface of composites and study the collaborative work of several layers with nanoscale thickness was tested and put into operation.



Figure 4. Vacuum station VUP-4

Integrated Rearch Institute of the Russian Academy of Sciences acquired instruments for the study of surface properties of macromolecular compounds (surface tension, corner moisturizing) by the drop method and plate method, which allow studying nanocomponents of liquid phase (Figure 5-8).

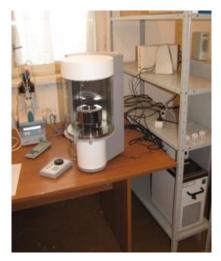


Figure 5. Tensiometer K-100



Figure 7. Langmuir balance



Figure 6. Automatic tensiometer DSA-100



Figure 8. Fine water filtering system

As noted above, currently there are several ways to improve the properties of composites using polymers:

- introduction of a small amount of polymer additives in the composite mixture (composites with polymer additives, including superplastificators, and cement-polymer composites);
- application of polymeric binder (polimer composites);
- soak treatment of concrete and ferro-concrete products with special polymer compositions or monomers with their further polymerization directly in the body of a composite;
- reinforcement by polymer fibers and micro-fibres;
- application of polymer lightweight aggregates or polymer modified aggregates in a composite;
- introduction of polymeric micro fillers to a composite;
- introduction of polymeric ultra-fine fillers to a composite;
- introduction of polymeric nano-additives to a composite.

Each direction has its own advanteges and rational applicable scope.

The use of various types of polymer additives in concrete has expended recently. The so-called superplasticizers prove very promising among those. Superplasticizers based on melamine resins (melment, 10-03 etc.), naphthalensulfonic acids (meitei, C-3, 30-03 etc.) and modified lignosulfonates are of the most common application.

Superplastizers are compounded into concrete mixture in the amount of 0.2-1.0% of binder weight. Superplastiziers contribute to significant dilution of the mixture composition while maintaining the proper fixity of mix and hydration kinetics of binder (fig. 9). They are a powerful tool for change of the rheological properties of mineral binder. The use of superplastizers for obtaining particularly high-strength composites or for improvement of concrete technology by applying cast concrete mixtures is considered the most advantageous. In our experiments the use of superplastiziers provided obtainment of M 600-M 700 concrete grades on the cement grade 400 and M 700-M 800 concrete grades on cement grade 500 (Bazhenov, 1983). The use of superplasticizers in combination with other methods of modifying composites by polymers, with soak treatment of a hardened composite by polymeric materials, in particular, which can achieve compression strength of over 300 MPa opens great opportunities.

Introducing polymer additives in a composite in the amounts of more than 2% of binder weight gives the so-called cement-polymer composites (fig. 10) (Bazhenov, 1983). In this case, the presence of polymer in composite affects properties of the material, especially on tensile strength and flexural strength, and behavior of composite in operating conditions. various latexes and certain types of pitches are used as additives. Effect from applying polymer additives is usually measured in tens of per cent compared to composite without any additives.

Polymer additives and superplastizers can be used along with other chemical additives as components of compounded complex additives that change the properties of composite and composite mixture in the right direction.

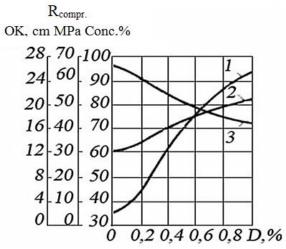


Figure 9. The influence of superplastizer content on the properties of composite and composite mixture: 1 - change of the mixture mobility after the introduction of superplistizer and ongoing flow of binder and water; 2 - increase of a composite strength at a constant mobility of mixture and binder consumption due to reduction of water consumption; 3 - reduction of binder consumption

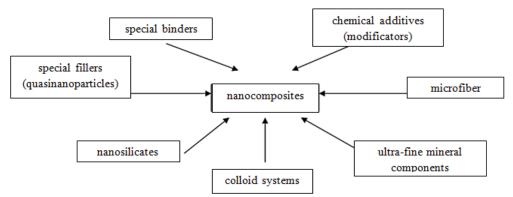


Figure 10. Structure of multi-component nanocomposites

Polymer composites are another big group of new composites. There are more than 30 types of polymer concretes both heavy and light (Bazhenov, 1983; Bazhenov & Mazhiev, 2011; Bataev et al., 2007; 2008; 2012; Mazhiev and Betilgiriev, 2012). The most widely used composites on resins are FAM, PN-1, UKS. Heavy polymer composites have compressive strength of 60-120 MPa, tensile strength of 5-10 MPa, permeability several times lower compared to conventional concretes, high chemical resistance and a number of other positive properties. Light polymer composites at an average density of 1500-1800 kg/m³, may be of 40-80 MPa in strength and 2-5 MPa in strength at an average density of 400-600 kg/m³.

Further improvement of polymer properties, reduction of creep and shrinkage, increased durability, as well as cost reduction, in particular, are important tasks of polymer composites development.

Application of polymer fibers as disperse armature needs improvement. The introduction of fibers into cellular and especially lightweight composites, as well as in gypsum composites is the most promising. In these cases increased deformability of composites favours their joint operation along with polymer fibers, which also have very high deformative properties. Consequently the strength of the material, its shock resistance and crack toughness increase, which is decisive in ensuring the seismic resistance of building structures.

Application of polymer lightweight aggregates, especially in combination with polymeric binder allows getting particularly lightweight heat-insulated materials resistant to moisture and frost and enabling creation of lightweight building constructions.

Polymer materials are used for filler modifications as well, for example for reduction of water absorption of lightweight fillers by creating a polymeric film on their surface or partial soak treatment of a filler. Polymer materials can also be used for improvement of adhesion between filler and binder, by grafting polymer on binder as well (for example, polyethylene fibres on expanded clay). However, ways of filler modifying by polymers have no use in construction, since the achievable effect does not often compensate for the increase of the cost of material and complicating the technology. Moreover, polymer materials are still scarce and their usage is appropriate primarily, where they can provide large techno-economic effect.

The scientific and research center for public use (SRCPU) of Grozny State Petroleum Technical University and Complex Scientific and Research Institute of Russian Academy of Sciences (SRCPU) conducted some sample tests of cement, nut ash, clay, alebaster, filler paste, including qausinanoparticles, nanosized colloidal particles and jellous thin layers on the surface of grains on the existing equipment

and facility testing stock (Bazhenov & Mazhiev, 2011; Bataev et al., 2008). The tests were conducted in high pressure autoclave (fig. 1) under the pressure of 150 to 500 ATM. The experiment was aimed at identification and studying the dynamics of changes of physico-mechanical properties of materials, including quasinanoparticles, nanosized colloidal particles and jellous thin layers on the surface of grains under high volumetric pressure. The samples were cylinder-shaped, except for the clay sample, which had a spherical shape. Cylinder diameters were within 1.7-2.0 cm, height – 1.8-2.0 cm, diameter of the clay ball – 1.68 cm. The tested components did not contain any complex additives and modifiers, which had a negative impact on the changing dynamics of properties. In the presence of complex additives and modifiers parameters of physico-mechanical properties of the tested samples were significantly higher.

Cylinders of identical size were made from the presented samples so as to compare test results: diameter is 16 mm, height 16 mm, cross-sectional area is 2.01 cm^2 , volume is 3.21 cm^3 . Cube with edges of 1 cm was made from the clay ball. The results of the test are as follows.

- At pressure $P = 150 \text{ kgf/cm}^2$, exposure time -16 hours.
- Nut ash: density 1.882g/cm³, 1.874 g/cm³, corresponding compressive strength 10.98 kgf/cm², 11.50 kgf /cm².
- Cement: density 2.077g/cm³, compression strength 154.67 kgf/cm².
- Alabaster: density 1.820g/cm³, compression strength 21.27 kgs/cm².
- Clay: density 2.14 g/cm³, compression strength 13.96 kgf/cm², water absorption - 1.4%.

At pressure $P = 400 \text{ kgf/cm}^2$, exposure time – 16 hours.

- Cement: density 2.177g/cm³, 2.240 g/cm³, 2.232 g/cm³, respectively, compressive strength 184.67 kgf/cm², 205.96 kgf/cm², 195.59 kgf/cm².
- Water absorption (10 hours of water soaking at temperature of 20° C) 0%. At pressure P = 400 kg/cm², exposure time 16 hours.
- Filler paste: density 1.73 g/cm³, 1.81 g/cm³, respectively, compressive strength - 19.44 kgf/cm², 20.10 kgf/cm².
- Samples from the nut ash have low compressive strength, collapsed under the pressure of 1.0 -2.0 kgf/cm².
- At pressure $P = 500 \text{ kgf/cm}^2$, exposure time -16 hours.
- Alabaster: density 1.880 g/cm³, compression strength 24.20 kgf/cm², density - 1.840 g/cm³, compression strength - 22.42 kgf/cm².

The analysis of the test results led to the following conclusions.

Cement – along with the pressure increase density rise, water resistance and compressive strength are observed. Cement density in the compressed state is 1.5-1.7 g/cm³, while the true density is 3.0-3.2 g/cm³. Clay – strength and density are increasing, sample surface becomes smooth, solid enough. Alabaster, filler paste – no significant pressure effects on the growth of strength has not been detected, the surface of the samples is saturated with liquid to a depth of 2-3 mm caused by depressurization, the structure is plastic.

Gypsum (alebaster) density - in the compressed state is 1.250-1.450 g/cm³, while the true density is 2.60-2.75 g/cm³. Ash – samples do not gain strength under pressure.

The increase of pressure results in occurrence of dense structure, i.e. material components are maximally packed, herewith in response to the substantial increase of the contact area quantum properties of small particles actuate, which are usually

uncommon for large-sized objects, which proves theoretical assumptions of academician V. I. Minkin (2008).

Conclusion

In conclusion, it should be emphasized that there are necessary conditions for research in the field of nanotechnologies and nanomaterials in the Chechen Republic. In this regard synthesis and study of polymer composites with predefined properties and functions deserves special attention. Research and development data should be noted among those perspective for the Chechen Republic.

It should also be noted that the solution to the problem of development of address modifiers, which include surfactants, nanoparticles and quasinanoparticles allows obtaining a large variety of construction nanomaterials with a wide range of properties and features, which is going to ensure the creation of new products, semifinished products, designs and details of buildings and structures, efficient technologies of their erection, and conditions for comfortable and safe life.

Disclosure statement

No potential conflict of interest was reported by the authors.

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