International Journal of Applied Engineering Research ISSN 0973-4562 Volume 10, Number 19 (2015) pp 40451-40453

Additive Based on Biosiliphycated Nanotubes

[1]N. Lukuttsova, [1]A. Ustinov

[1]Institution of Higher Education Bryansk State Technological University of Engineering (BSTU)
3StankeDimitrova str., Bryansk, 241037, Russia natluk58@mail. ru, allexian@mail. ru

Abstract
The paper presents the results of the study of the nano-disperse additive for concrete, mortar, ceramics and other building materials based on biosiliphycated nanotubes of cyanobacteria of Leptolyngbya sp. 0511, Leptolyngbyalaminosa 0412, Leptolyngbya sp. 0612 of Lake Baikal (Russia). It is established that the average diameter of the obtained nanotubes is from 61 to 4 384 nm. Different kinds of stabilizers ensuring stability of the nano-dispersed additives are tested. The photon correlation spectroscopy has proved that the dependence of the size of biosiliphycated nanotubes and the stability of disperse phases of suspensions in the water media of stabilizers S-3 superplasticizer and polyvinyl alcohol on the ultrasonic dispersion time is extreme. The ultrasonic dispersion time of 10 minutes optimal for suspending of biosiliphycated nanotubes with minimal particle size is fixed.

Keywords: cyanobacteria, biosiliphycated tubular formations, ultrasonic dispersion, stabilizers, biosiliphycated nanotubes, nanodispersed additive for concrete, mortar and ceramics

Introduction

At present the possibility of intentional formation of dense and defect-free structure at the micro- and nanolevel is a necessary condition for creation of high-strength composite building materials for constructional and decorative purposes. This condition can be fulfilled by using highly active nano-dispersed additives acting as centers of extra crystallization that strengthen new formations in the pore space of concrete and mortar [1, 2].

The most common synthesis methods of the majority of nano-disperse additive compounds for composite materials are technologies characterized by the use of costly and energy-intensive equipment, high pressure and temperature, plasma and arc discharge, as well as toxic reagent with multi-stage chemical treatment. This leads to a significant increase in the cost of this type of additives and prevents their widespread introduction.

Cyanobacteria are a significant group of large gram-negative bacteria of 0. 1-2. 0 micron of the thermal springs of Baikal Rift Zone [3].

Synthesis of nanoparticles with biological sources is of great interest due to a number of advantages over traditional technologies. Bacteria, viruses and algae are biological objects.

The aim of the work is to study the nano-dispersed additives based on biosiliphycated nanotubes, obtained in the form of suspensions by ultrasonic dispersion of biosiliphycated tubular structures in the water media of organic stabilizers.

The experimental part

In the study the following materials were used.

The dispersion medium for suspension is mixture of cyanobacteria species *Leptolyngbya* sp. 0511, *Leptolyngbyalaminosa*0412, *Leptolyngbya* sp. 0612; organic stabilizers: S-3 superplasticizer as dry substance (PLC «Polyplast», Novomoskovsk, Tula Region); and polyvinyl alcohol (PVA) of 16/1 brand (PLC «Scientific Production Company ErmakChem», Moscow); distilled water; chemical agents for nutrient medium (RussChem LLC, Moscow);

The basis of S-3 superplasticizer is sodium polynaphthalenemethylenesulfonates or methylenebis (naphthalensulfonates) of various molecular weights, obtained by polycondensation of naphthalene sulfonic acids with formaldehyde and following neutralization with sodium hydroxide. Polynaphthalenemethylenesulfonates are linear polymers with reiterating sulfate groups at regular intervals. Polyvinyl alcohol $[–CH_2CH(OH)–]_n$ is a tamely ramified polymer with relative molecular mass of $(5…200)\cdot10^3$ and remanent acetate groups in macromolecules.

The culture of cyanobacteria was grown in the synthetic medium Z-8 in the bioreactor with the ammonium chloride at fixed light and temperature of 25°C, introducing micro-dispersed metasilicic acid into the nutrient medium. Biosiliphycation lasted from 10 to 28 days. After this time, the culture was treated with heat in the oxygenated water of 37% concentration for 0. 3 hour at 70°C. Then this mass was washed out in the distilled water and dried [4].

The obtained white powder containing biosiliphycated tubular formations was studied by X-ray phase analysis (diffractometer ARL X'TRA), photon-correlation spectroscopy (ZetaPlus with the system 90Plus/Bi-MAS), electron microscopy (Microscope Quanta 3D FEG). Nanodispersed additive production was carried out in two stages. The first stage was intergrinding (in the laboratory mill) mineral and stabilizing components taken in a ratio by weight of 1 : 0, 5 to the powder with particle surface area of 360-380 m^2/kg. The second stage was dispersion of this powder with the ultrasonic bath-type activator in the aquatic environment for 5-30 minutes at ultrasonic frequency of 35 kHz, solid phase concentration of 5-15%, temperature (20 ± 2) °C. The ultrasonic dispersion of biosiliphycated tubular structures in the water media of organic stabilizers was performed in the impulse bath-type activator PSB-4035-04.

Results and Discussion

The study of the obtained powder of biosiliphycated tubular structures by X-ray phase analysis showed that it is mainly

composed of oxygen (44. 15%) and silicon (46. 66%), and it also contains carbon (6. 77%), sodium (1. 13%), magnesium (0. 74%) and phosphorus (0. 55%). The cyanobacteria remains affirm the presence of carbon in it.

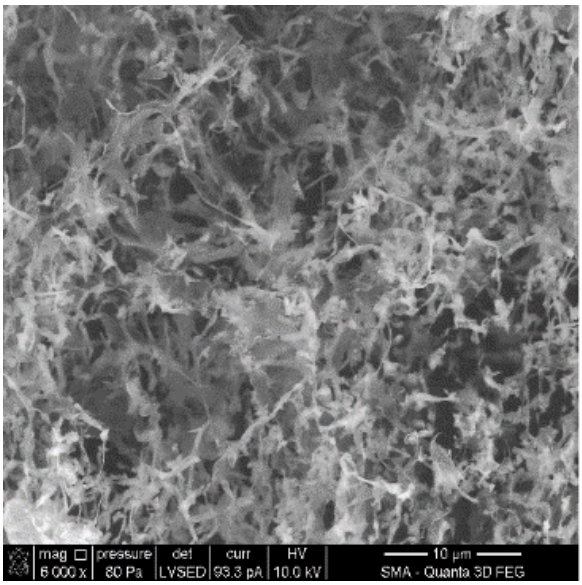
There is interweaving of merged biosiliphycated tubular formations in the photograph taken in the water media (Fig. 1a), as well as separate caps (hollow tubes) consisting of amorphous silica (Fig. 1b). Such tubular structures have a clearly distinguishable mouth and a siliceous cap. The diameter of the tubes is from 61 to 4000 nm and the length is from 1000 to 4384 nm.

Nanodisperse additive was obtained by ultrasonic dispersion in the water media of merged biosiliphycated tubular structures [4]. It is established that the ultrasonic dispersion facilitates the separation and destruction of the interwoven biosiliphycated tubular formations and production of nano- and micro-dispersed objects of 3 types of 61-4384 nm in size: nanotubes and their units, fragments of tubular structures and aggregated silica particles.

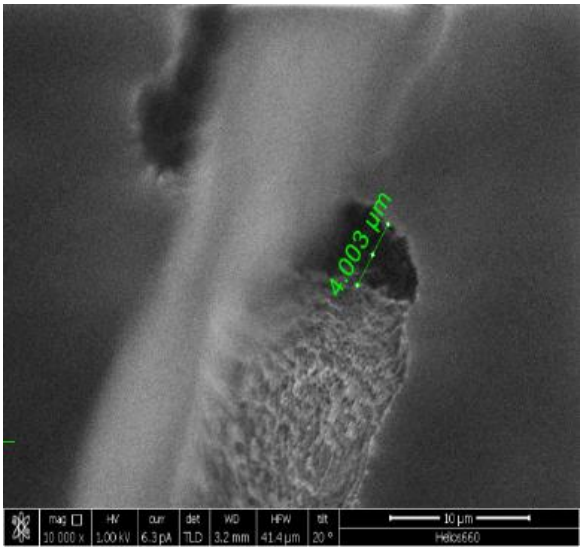
In order to increase the aggregative stability of the highly disperse systems based on biosiliphycated tubular formations in the water dispersion media, the influence of stabilizers (S-3 superplasticizer and polyvinyl alcohol) various by action mechanisms and at the same time the most common ones were investigated.

The photon correlation spectroscopy has showed that the dependence of the particle size and the stability of the disperse phases of suspensions of biosiliphycated nanotubes stabilized by S-3 superplasticizer and polyvinyl alcohol on the ultrasonic dispersion time is extreme (Table 1), while the ultrasonic dispersion time of 10 minutes is optimal for suspending of biosiliphycated nanotubes with minimal particle size.

It is established, that the ultrasonic dispersion of biosiliphycated tubular structures in the water media without stabilizers results in suspending with dispersed phases being aggregately unstable (Table 1). It is affirmed by the average ζ-potential of the dispersed system (-3. 48 mV), which is below critical (-30 mV), while ζ-potential for stable systems ranges ± (30 - 70) mV [5].



a



b

Fig. 1. BiosiliphycatedTubularFormations in the Water Media:

a) interweaving of merged biosiliphycated tubular formations, x6000.
b) biosiliphycatednanotube (cap), x10000.

At the ultrasonic dispersion suspensions of biosiliphycated nanotubes with the presence of S-3 superplasticizer for 5-10 minutes, the average particle size decreases from 448 to 320 nm at their minimum size of 61 nm, and the particle size increases from 320 to 502 nm when the dispersion time is increased from 10 to 15 minutes.

The analysis of ultrasonic dispersion time effect on ζ-potential of suspensions of the dispersed phases, stabilized by S-3 superplasticizer has shown that their sustainability to the aggregation increases progressively with the increase of ultrasonic dispersion time from 5 to 10 minutes, as evidenced by the change in the average value of ζ-potential from -38, 5 to -74, 2 mV. The S-3 stabilization effect is mainly due to the fact that the adsorption layers increase the absolute value of the ζ-potential, i. e. aggregate stability of the particles is provided chiefly by their electrostatic repulsion.

Ultrasonic dispersion of biosiliphycated tubular formations in the water media of polyvinyl alcohol for 5-10 min results in suspending, with the average particle size decreasing from 7 136 to 3 830 nm and 1450 nm minimum, and when ultrasonic dispersion time increases from 10 to 15 min it grows from 3830 to 4510 nm. Further time changes of ultrasonic machining from 10 to 30 min is not reasonable as it leads to aggregation of the particles and the formation of aggregates with particle size up to 39910 nm. At that, ζ-potential varies insignificantly from -38, 5 to -44, 4 mV. However, as our previous researches showed, the factor of electrostatic repulsion does not matter for nonionic high-molecular stabilizers including polyvinyl alcohol [6].

It should be noted that the use of polyvinyl alcohol as a stabilizer leads to long adsorption layers, that increases the size of the particles of the dispersed phase from 320 to 3830 nm compared to S-3, i. e. more than 10 times, and the

aggregate stability is provided mainly through the adsorption-solvation and structural-mechanical factors. On the surface of the dispersed phase of biosiliphycated nanotubes there are -OH groups, as a result, of reacting with the water media, so the character of the adsorption interaction between the solid surface and macromolecules of polyvinyl alcohol is substantially determined by hydrogen bonds between -OH surface groups and -OH groups of the polyvinyl alcohol.

Table 1. The Particle Sizes and Stability Indicators of the Disperse Phase of Suspensions of BiosiliphycatedTubes a Day AfterUltrasonic Dispersion

Suspension of biosiliphycated nanotubes		Particle sizes in the dispersed phase, nm		
Stabilizer	Time of the ultrasonic dispersion, min	mini-mum	maxi-mum	average
Without stabilizers	10	438	4384	1249
	15	381	1834	593
S-3	5	259	972	448
S-3	10	61	742	320
S-3	15	81	915	502
PVA	5	2135	11651	7136
PVA	10	1450	5530	3830
PVA	15	1560	10914	4510
PVA	20	3197	26185	6400
PVA	30	4660	52200	39910

Conclusion

The studies has shown that ultrasonic dispersion contributes to obtaining of nano- and micro-dispersed objects of 3 types of 61-4384 nm in size: nanotubes and their units, fragments of tubular structures and aggregated silica particles.

It has been established that the dependence of the particle size and the stability of the disperse phases of suspensions of the biosiliphycated nanotubes stabilized by S-3 superplasticizer and the polyvinyl alcohol on the ultrasonic dispersion time is extreme.

The photon correlation spectroscopy has determined the ultrasonic dispersion time of 10 minutes being optimal for suspending of biosiliphycated nanotubes with minimal particle size.

References

[1] Lukuttsova N. P., Pykin A. A. Theoretical and Technological Aspects of Production of Schungite-based Micro- and Nano-disperse Additives to Concrete. Bryansk, 2014.

[2] Lukuttsova N., Luginina I., Karpikov E., Pykin A., Ystinov A., Pinchukova I. High-Performance Fine Concrete Modified with Nano-Dispersion Additive. International Journal of Applied Engineering Research (IJAER), v. 9, № 22, pp. 16725-16733, 2014.

[3] Sorokovnikova E. G. Study of Cyanobacteria Silication by Means of Chemical Analysis and Electron Microscopy E. G. Sorokovnikova, E. N. Danilovtseva, V. V. Annenkov. Abstr. of the IV Congress of the Russian Society of Biochemists and Molecular Biologists, Novosibirsk, 2008.

[4] Patent of the Russian Federation 2539734, IPC C12N B82B. The Method for producing of biosiliphycated nanotubes. Lukuttsova N. P., Ustinov A. G., Appl. 22. 11. 2013, Publ. 27. 01. 2015.

[5] Frolov Y. G. The Course of Colloid Chemistry: Surface Phenomena and Disperse Systems. M., 2009.

[6] Lukuttsova N., Pykin A. Stability of Nanodisperse Additives Based on Metakaolin // Glass and Ceramics, v. 71, № 38, pp. 383-386, 2015