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NANOMODIFICATORS BASED ON CAVITATIONALLY ACTIVATED WOOD CARBON-BLACK

Olesya P. Stebeleva, Lyudmila V. Kashkina, Vladimir A. Kulagin, Tatyana Y. Emelyanova
Siberian Federal University, Russia, Krasnoyarsk

Abstract

The purpose of this paper is the research of hydrodynamic cavitation effect on structure and physical properties of cavitationally activated carbonaceous materials (CACM). The hydrodynamic rotor mixer has been used for rather short cavitation processing of the weak water suspension of wood carbon-black. Using CACM as a nano modifier improves the physico-mechanical properties of building materials and lubricants like fullereniferous carbon-black.

Key words: *nano modificators, carbon-black, cavitation effects*

The considerable material and energy costs for the synthesis of nanotubes, fullerenes, nanodiamonds cause its high cost. Therefore, searching for new environmentally-friendly energetically favorable production technologies carbon and other nanomaterials is a crucial task as well as achievement of industrial effects when using these materials as a modifier in a quite narrow concentration range. This paper presents the results of study capacity hydrodynamic processing of powder materials varying dispersion and modification of the properties of building, lubricating compositions by carbon materials based on wood carbon black produced by cavitation effects, with allows expanding the field of use.

It is known that the velocity of the phase boundary at a cavity microbubble collapse can reach 500 m/s and depends on its radius. The collapse of the bubble goes on within submicroseconds. The temperature in this local spot rises up to 10^3-10^4 K as a result of adiabatic compression.

At the cavity bubble collapse in the local volume inside and near to it there are generated fields of high pressure (up to 2000 MPa). The phenomenon is accompanied by intensive turbulent micromixing and mechanical thermolysis of water with the formation of H_2, O_2, H_2O_2 and free hydrogen bonds. The pulsation effects of cavitation turn each bubble into a cavitation microreactor in wich there are created preconditions for reactions to go. Thus, high local pressures and temperatures make it possible to consider hollow cavitations as an peculiar energy generator which for rather a long time of the cavity expansion from a nucleus, accumulates energy and during the collapse generates it into surrounding fluid [1].

The results of dispersing 0.1% aqueous suspension of ultra-dispersed diamonds (UDD) produced by detonation synthesis using hydrodynamic generator and surfactants diamonds are shown in paper [2]. As a result particle size reduction by more than 25% was observed after treatment (132 nm). Effective scattering size of the UDD before dispersion - 170 nm (Fig 1).

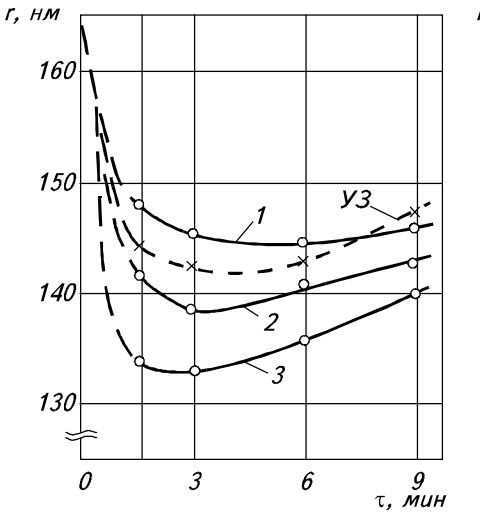


Fig. 1 Time course of ultrasonic processing (УЗ) and hydrodynamic dispersion (with the rotation mode 1 – 2000 rpm, 2 – 4000 rpm, 3 – 7500 rpm) on the radii of UDD [2]

Dispersing was carrying out in hydrodynamic rotor mixer with wedged two-bladed stirrer in supercavitation mode. Engine power - 1kW, volume of the working chamber - $3 \cdot 10^{-4}$ m^3, rotor speed 10000 r/min. Concentration of the aqueous suspension for the ash 3 and 25% for carbon black - less than 1%wt. After processing, obtained suspension containing studied powders as a disperse phase was dried in the air at t = 25 °C in Petri dishes (Fig. 2, 3).

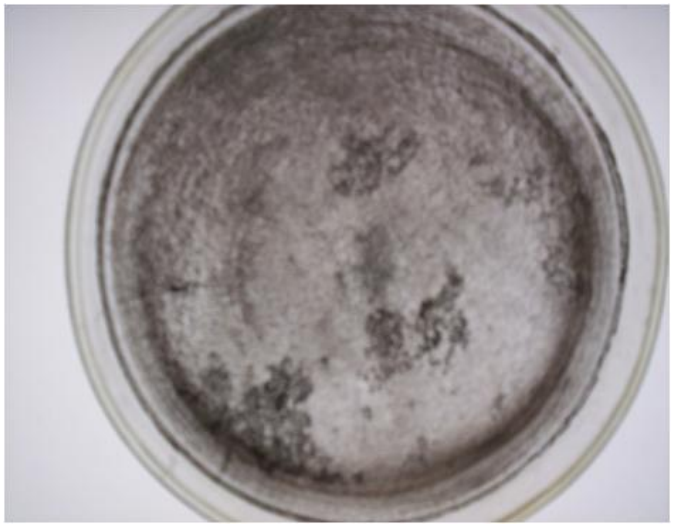
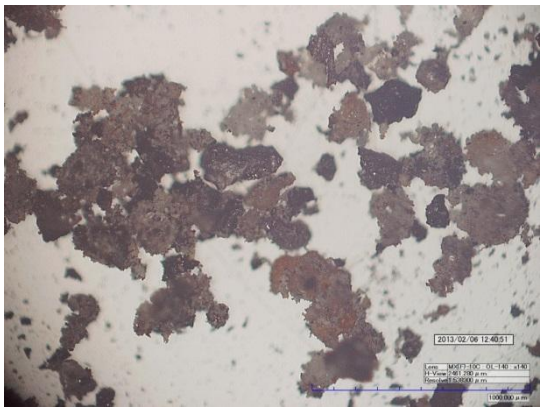


Fig. 2. View of carbon black after dispersing in Petri dish


a)

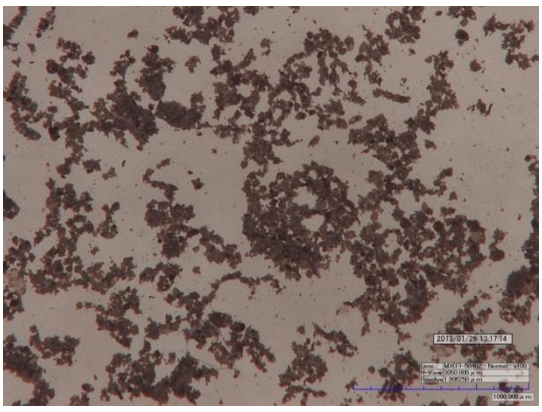
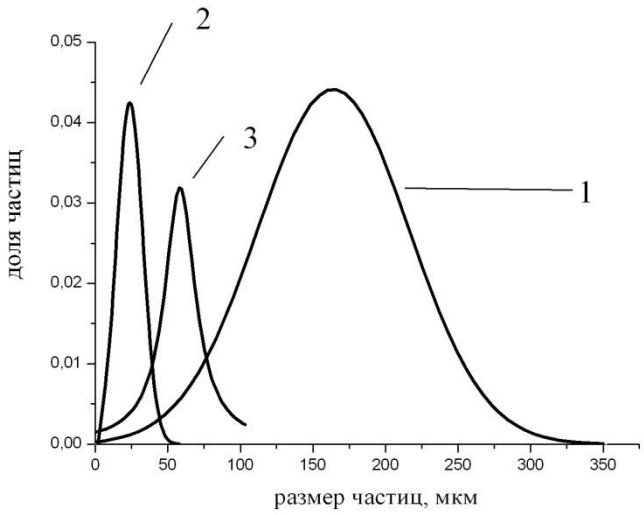
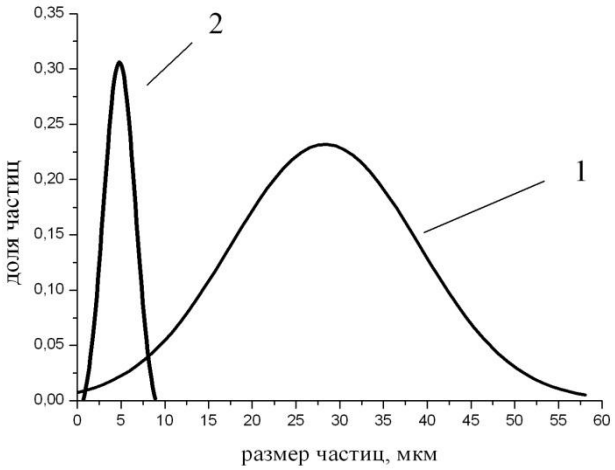

b)

Fig.3. Optical micrographs of the powder (microscope HIROX KH-7700) initial ash (a) and ash after dispersing (b)

It was understood that ash dispersed in a 25% suspension, a decrease average particle size by 40% and for 3% particle sizes reduce by 7 (Fig. 4a).



a)



b)

Fig. 4. Particle distribution size of ash: a - initial ash, average particle size 175 um (1), ash after the dispersing 3% wt. suspension (2), ash after dispersing 25 wt%. suspension (3), b - initial ash, average particle size 25 microns (1) ash after dispersing 3% wt. suspension (2)

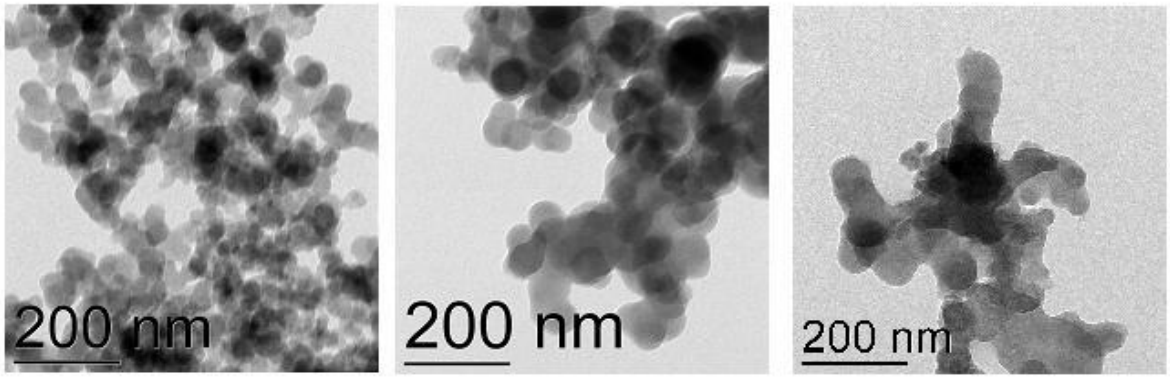
The average particle size after processing will be 3.5-4 um after dispersing of ash with average initial particle size 25 um at the same conditions (Fig. 4b).

In work [3] it has been shown that the hydrodynamic dispersion of the low-concentration aqueous suspension of the wood carbon black enable obtaining the carbon material containing small concentrations of fullerenes C_{60}, C_{70} (cavitationally activated carbonaceous materials, CACM) due to cavitation effects (Tab. 1).

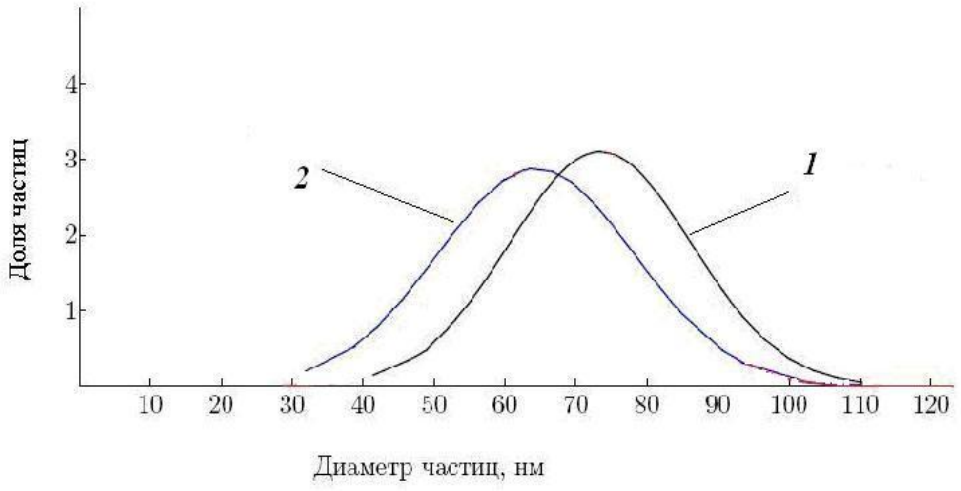
Tab.1. Values of interplane distances d_{hkl} for CACM and C_{60}

№ of line	Table data ASTM C_{60}						Experimental data	
	1990		1991		1994		CACM	
	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I
1	8,1800	100	8,1464	100	8,1596	100	8,1715	82
2	4,2800	65	4,2543	63	4,2720	70	4,2932	90
3	4,1100	10	4,0732	14	4,0901	15	4,08874	90
4	3,1800	10	3,1550	10	3,1630	14	3,15981	90
5	2,9000	5	2,8801	8	2,8931	10	2,87603	100
6	2,7400	5	2,7154	8	2,7263	9	2,74983	80
7	-				2,5047	1	2,51722	70

Change of size-consist with a decrease in the average particle size is a result from cavitation processing at the same condition as for ash, the average particle size for wood carbon black 73.5 nm, for CACM - 63.5 nm (Fig. 5).



a) *b)*

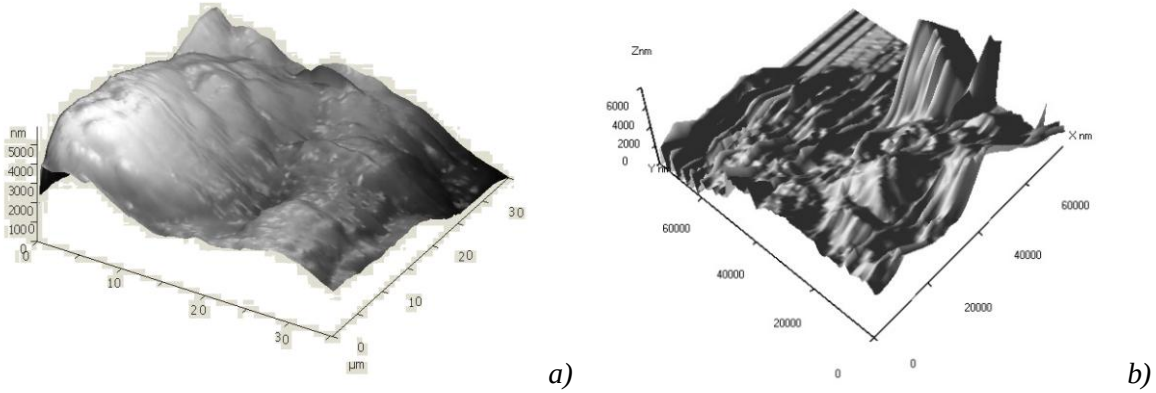


c)

Fig.5. Electron micrographs of the powder (electronic microscope JEOL JEM-2100) wood carbon black (a) and CACM (b); c - the density function of the wood carbon black (1) and CACM (2)

Top-down nanodispersed material behaves as an active nanomodifier in various industrial processes. Effect of the extrudant CACM on the strength characteristics of cement and concrete was studied [4]. Test samples of cement and concrete were prepared with a constant water-cement ratio and the equal concentration of modifier <1% wt. Samples of concrete containing a river sand with a particle size from 0.14 to 5 mm. as aggregate. It has been found experimentally that on addition of CACM in an amount <1 % wt microhardness for samples of cement increase by 1.7 compared to the cement sample without CACM and provide the appearance of fibrillar structure of cement (Fig. 6). Adding CACM with different time interval between the preparation and the use of (1 and 6 months) with

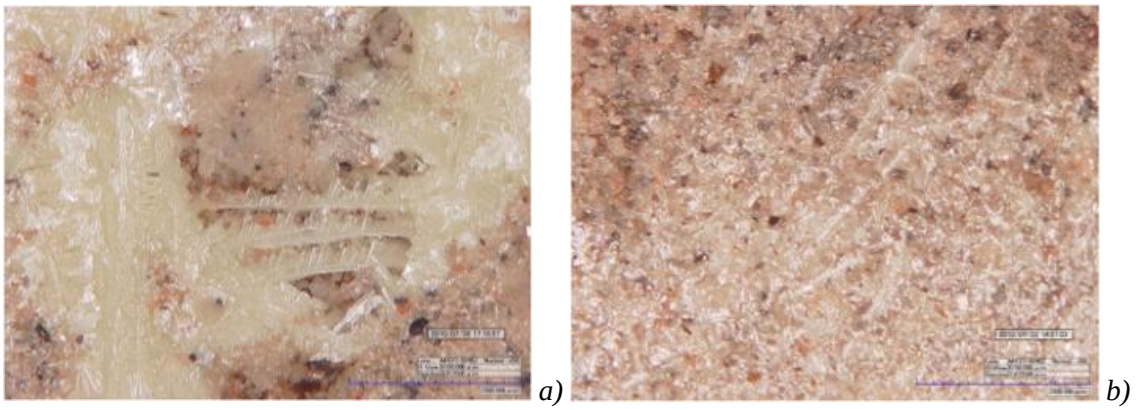
concentrations <0.1% wt. to the concrete composition increases the compressive strength of the resulting sample, compared with a control sample by 60%.



a) *b)*

Fig.6. The morphology of unmodified cement (a) and cement with fibrillar structure modified by CACM (NanoEducator Scanning Probe Microscope)

Sulfur concrete compositions were made with a ratio sand and sulfur 60:40 (%).CACM-modified composition was prepared in such a way as to maintain the overall ratio of sand and sulfur. Sand-sulfur blend modified CACM heated to 140 ° C, at constant stirring and held for 1 minute poured into molds. Structural characteristics of sulfur concrete samples were investigated by Vickers microhardness test. Microhardness of sulfur concrete samples containing CACM less than 1% wt. increased over 35%, and 16% in the sample containing CACM more 1 % wt. compared to the sample without CACM. Surface microscopy of sulfur concrete samples showed that the CACM as a modifier increases a crack resistance of sulfur concrete (Fig. 7).



a) *b)*

Fig.7. Surface of sulfur concrete without CACM (a) and surface of sulfur concrete modified by CACM (b) (microscope HIROX KH-7700)

Preparation of lubricating composition was carried out by adding CACM powder, beforehand dissolved in a drop of petrol into 50ml of industrial oil I-20A, followed by accompanied mechanical

agitation for 1-2 minutes. As follows from the experiments on the friction machine CT-2 with a test pair steel SH15 - steel 45 (pedestal bearing), load P = 25H, speed 800 r/min. adding CACM with low weight concentrations into industrial oil I-20A leads to a significant (almost twice) wear reduction of steel friction surfaces. It is worth noting that concentration of the added powder an order less than concentration of friction modifier (fullerenes, fullerene-containing carbon black) described in the literature [5].

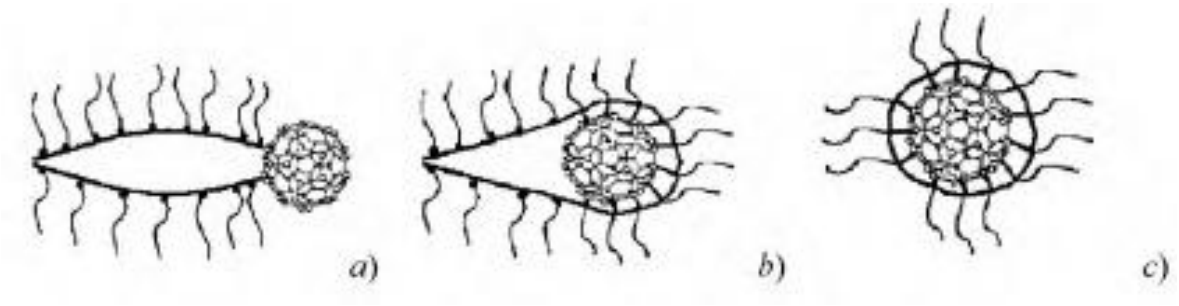


Fig. 8. Diagram of the crack extension across a polymer matrix modified with C_{60} molecules. a - initial stage, b - covalent bonds formation and partial retraction of a C_{60} molecule into the microcrack, c - complete retraction of the C_{60} molecule into the microcrack

In work [6] they suggested a hypothetical mechanism of hardening effect of fullerene carbon-black at friction. The electron shells of fulleroids are characterized by the presence of a great quantity of delocalized %-conjugate electrons. A mechanical destruction of polymer chains is effected under mechanical destruction of the polymers in the mouth of generated microcracks. Apparently an analogous process takes place in the mouths of numerous microcracks resulting in wear particles formation. Fig. 8 gives a diagram of the crack extension reaching the C_{60} molecule (or small conglomerate). Free polymeric radicals concentrate on the microcrack surface (Fig. 8 a). Some of them having reached the fullerene surface, forms with fullerene. On further increasing the forces that open the crack, these bonds split and there occurs retracting a C_{60} molecule (or aggregate of molecules) into the microcrack (Fig. 8 b), going with generation of a greater number of new covalent bonds of polymeric radicals with fullerene that finally results in «healing» the microcrack (Fig. 8 c).

Thus, our studies have shown that the used low-capacity rotor hydrodynamic generator allows reducing the ash particles by 7. But the concentrations of the working suspension should not exceed 3% wt. The dispersion effect is much less at higher concentrations of suspension. The hydrodynamic dispersion method method, rigid by cavitation effects and used in the materials processing can be successfully applied for the preparation of cheap carbon black-based modifiers. The research results revealed that CACM is effective as a nano modifier in various industrial processes.

Electron-microscopic research has been carried out in the laboratory of electronic microscopy of the Collective Using Center of Siberian Federal University.

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