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Electrical Conductivity and Aggregation of Carbon Nanotubes in a Heterogeneous System Based on Cement

Alexander Nikolaevich Lopanov,
Evgenia Aleksandrovna Fanina and Kalchev Dmitrii Nikolaevich

Belgorod State Techological University Named After V.G. Shukhov, Russia,
308012, Belgorod, Kostyukova St., 46

Abstract: A model for the electrical conductivity of heterogeneous systems based on cement and carbon nanotubes (CNT) is shown. The electrical properties of heterogeneous variances depend on several key parameters. The most important of these are such as the degree of aggregation of conductive particles and the electrical conductivity of a single unit. When the threshold concentration of electrical conductivity of CNT and graphite dispersions equal to 0.15, in systems with the electrical conductivity of CNT's systems are 5 – 6 times higher than graphite. It is shown that the carbon nanotubes have anomalous properties in comparison with graphite electrical dependencies due to the size and shape of the particles. It is suggested that the small size effect of CNTs on the primary aggregation and the elongated shape of the particles affects the concentration at which a significant increase in electrical conductivity. Small CNT concentration (0.005 – 0.007 wt.) is cause of strength characteristics reducing of silicate composite materials compared with graphite.

Key words: Model conductivity % Carbon nanotubes % Control electrical properties % Strength characteristics electrically conductive silicate composites

INTRODUCTION

Physico-chemical and performance properties of concrete (strength, chemical resistance, cold resistance, etc.) can be significantly improved by the addition of different materials. Thus, the introduction of fiber can improve concrete durability and improve fire resistance, abrasion resistance and cracking.

It is believed that the reinforcement of carbon nanotubes will get a new class of composite materials [1] and therefore represents a particular scientific and practical interest to study the conductive properties of concrete reinforced with carbon nanotubes. This is due not only to the fact that no detailed study their electrical properties, but also allow the regulation of the structure and properties of a large number of building materials and products for special applications.

The aim of this study was to investigate the electrical conductivity of cement with the addition of nanotubes.

Research objects and methods of measurement. As of the model system was used CNT – cement stone. The diameter of the hollow carbon fibers obtained by the catalytic decomposition of hydrocarbons is from 20 to 200 nm. Specific surface area as determined by low temperature nitrogen adsorption method (BET) is 90-120 m^2/g. The particle size distribution examined by laser Microsizer C-201 Fig. 1. The graphite grade GS-2 (GOST 17022-81) was used. The cement was used as the solid matrix. Cement properties are shown in Table 1.

Table 1: Chemical and mineralogical composition of the studied cement PC 400 (CEM I 42,5 N)

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	CaO (not binded)	Etc
Content, wt. %	22,4	3,72	3,43	66,2	3,61	0,11	0,35	0,18
Mineralogical composition of cement clinker								
Main components		C_3S		C_2S			C_3A	C_2A
Content, wt. %		61		18			5	16

Corresponding Author: Alexander Nikolaevich Lopanov, Belgorod State Techological University Named After V.G. Shukhov, Russia, 308012, Belgorod, Kostyukova St., 46

Samples for measurement were prepared as follow methods: in the aqueous phase of the nanotubes cement slurry was added to a normal density (the content of the aqueous phase is 30%). The suspension was stirred until it becomes homogeneous, the samples were cured for 30 days. For measurements shaped cylindrical samples with a diameter 2.10^{-2} m in length 1.10^{-2} m, the samples were dried at 200°C. Measurements of electrical conductivity was performed using an AC bridge at a frequency of 1000 Hz.

Problematic aspects of the research. Simulation of the electrical conductivity of disperse systems is carried out for a long time. Thus, in a works of Frick has been attempted to build an adequate model in which the dispersed particles are in the form of spheres [2]. In the future, the models become more complex and corrected on the basis of the laws of the constants for the calculation of the electrical conductivity of suspensions of nanoparticles [3, 4]. It should be noted that it is often created in the models do not take into account the parameters of particle aggregation. Problem of aggregation of particles conducting electricity is difficult mathematical task, as dispersions aggregation parameters change with the concentration of dispersions.

In connection with the development of new composite materials based on carbon nanotubes the interest is growing in the study of electrical conductivity of dispersions of carbon materials as well as ill-defined relationship between the microstructure and physico-chemical properties of the composite [5, 6]. Most of the studies of the electrical properties of materials with the addition of carbon nanotubes held for the organic polymer composites [7]. It is found that addition of surfactant, ultrasonication treatment of systems reduces the degree of aggregation of carbon particles.

Currently, a wide range of conductive composite materials for different purposes on the basis of carbon materials - graphite is developed. The basis for the synthesis of these composites is the regulation of electrical properties of the dispersions, which is necessary to understand the mechanism of transmission of electric current, converts it into heat energy. As conductive component often used various modifications or graphite or carbon (soot, fossil coal) having sufficient electric conductivity [8]. Thus, at the developed model, the electrical conductivity of a heterogeneous system takes into account the factor of aggregation of carbon particles [9 - 11]. The model can not only predict the electrical conductivity of the system, but also to carry out calculations of the thermodynamic parameters of particle aggregation.

It should be noted, that fractal model of the structure of various forms of carbon is widely used [12].

Great interest is the study of electrical properties of the elementary forms of carbon – fullerenes, carbon nanotubes (CNT) and the comparison of these materials with the traditional – graphites, carbon blacks [13]. Nanotube (ideal structure) is rolled into a cylinder cavity graphite surface laid by regular hexagons of carbon atoms. The properties of such systems depend on the angle of orientation of the graphite plane relative to the axis of the cavity. The orientation angle determines the chirality of the system, which determines, in particular, its electrical characteristics.

It appears, due of it's the electrical properties nanotubes are promising materials in the electronics industry for the manufacture of field effect transistors, power converters, functional devices having a wide range of properties. Thus, applying a reverse voltage of a few volts, you can change the conductivity of single-walled nanotubes by 5 orders of magnitude and to vary the thermoelectric voltage of carbon deposits [14, 15].

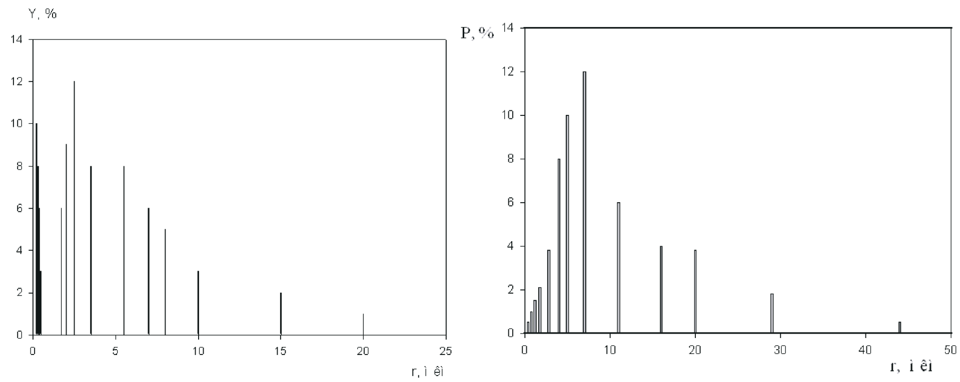
The need to control the electrical properties of the carbon-based composites, the objective of the study was to aggregation processes nanotubes in solid dispersion medium.

The study results suggest that the nanotube particles are aggregated in aqueous phase, Fig. 1. The quantity of units is within the 1000 – 2000 nm. We observed two peaks in size distribution of aggregates with peaks of 0.2 microns and 2–5 microns.

Fig. 2 shows the experimental dependence of the electrical conductivity with the mass fraction of CNT and graphite.

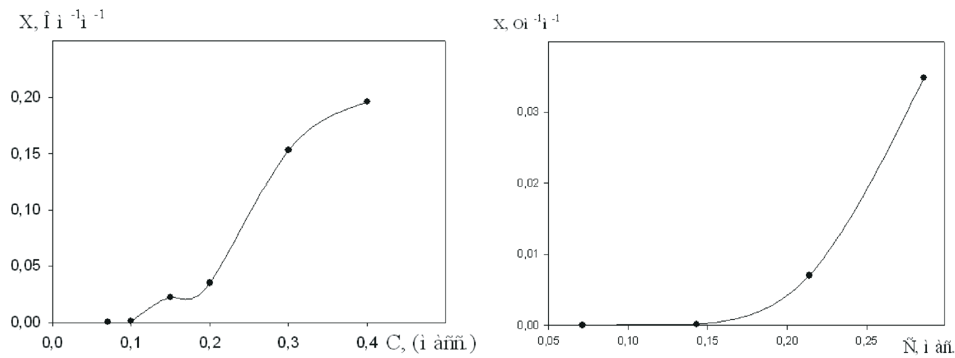
Functionally, the dependence of the electrical conductivity of graphite dispersion is significantly different from the system with carbon nanotubes, which can be explained by the specific structure of the nanotubes, which, like the long surfactant molecules are aggregated by individual fragments. When the mass fraction of CNTs is less than 0.2 degree of primary aggregates is up to 200 nm.

With an increase in the mass fraction of the conductive component the secondary aggregation has been taken place and the aggregates, which shape is close to sphere, form chains of 2 to 7 microns, Fig. 3.



A) B)

Fig. 1: The distribution of particle aggregates CNT (A) and graphite dispersions (B) in size



(A) (B)

Fig. 2: The dependence of the electrical conductivity (X) of CNT – cement stone (A) and graphite – cement stone (B) with the mass fraction of the electrically conductive substance, T = 293 K

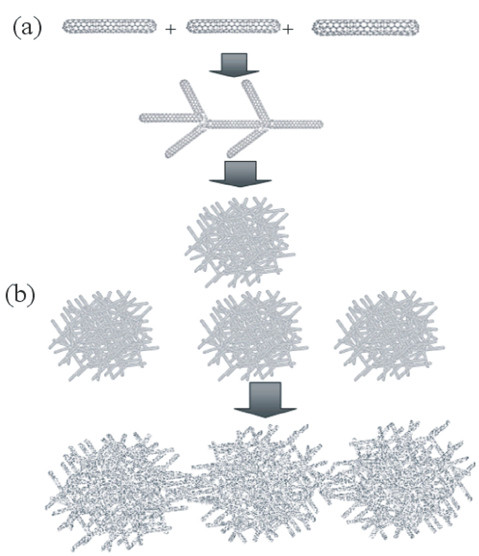


Fig. 3: Scheme of the chain-like structures of carbon nanotubes formation:
a) the formation of chain-like structures, b) the formation of three-dimensional microspheres

Studies of the structure of cement made by microscopy, also confirm the presence of aggregates in the heterogeneous system. In the micrographs one can observe dimensional microspheres formed of a plurality of nanotubes and chain structures of the aggregates of carbon nanotubes, Fig. 4.

High mass fractions of CNT (> 0.3 wt.%) corresponds to the curve plateau which showing that the resistivity is only slightly dependent on the concentration.

Simulation and experimental data processing was performed by the method described in [11]. For example, if the number of particles N, involved in the formation of aggregates is sufficiently large ($N>>10^6$), to apply the mathematical representation of the process and the law of mass action to the equilibrium state of aggregation of a formal scheme can be written as:

$$vX = Y.$$

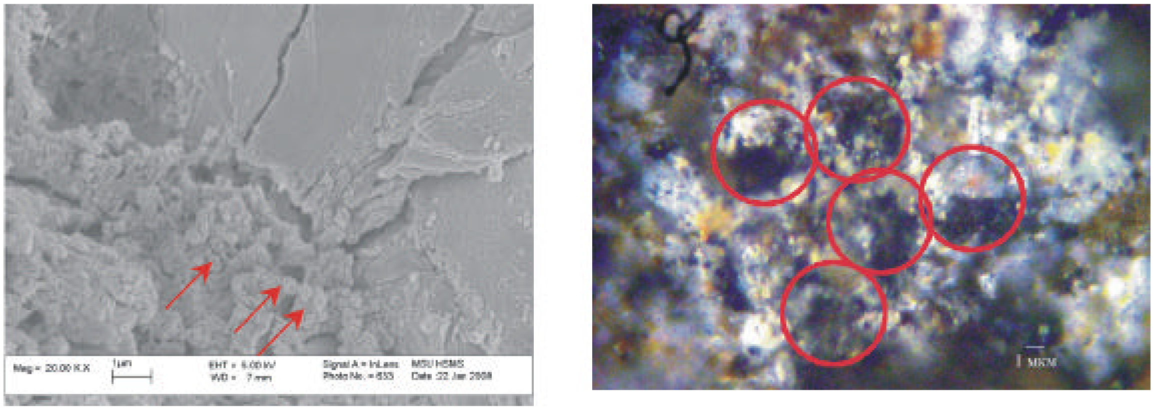


Fig. 4: Micrographs of carbon nanotubes aggregates in cement stone. Concentration of disperse phase is 0.007 wt, %

Here, *[Nu]* - the number of particles participating in the formation unit; *X, Y* - designations particles and aggregates.

Follow to the formal scheme, the equation for the equilibrium constant K is given by:

$$K = [Y]/[(N-\nu Y)]^{\nu},$$

where in [Y], [(N-νY)] – respectively, the concentration of aggregates of particles, N – initial particle concentration 1/m^3.

For small degrees of aggregation N>>νY, so the number of units conducting electric current is proportional to the initial concentration of particles N in the degree of [*Nu*]. Assuming that the electrical conductivity of single chain unit is equal to [*sigma zero*], we obtain the equation for the electrical conductivity of heterogeneous systems:

$$F = F_0 \bullet K \cdot C^{\nu}.$$

Analyzing the equation it may be noted that when the condition N>>νY dependence ln*F* from lnC should be linear. Using the equation $F = F_0 \bullet K \bullet C^{\nu}$, using the least squares method determines the number of units in the primary aggregation: the parameters ln (K*F*0) = 7,1; ν = 9,7; correlation coefficient was 0.99, which allows to suggest the adequacy the model used.

With small amounts of carbon nanotubes (0.1 wt.) the electrical properties of the cement composite is changing, due to the high conductivity properties of the nanotubes. This effect is due to the specific structure of CNT as a result they do not form an additional contacts,

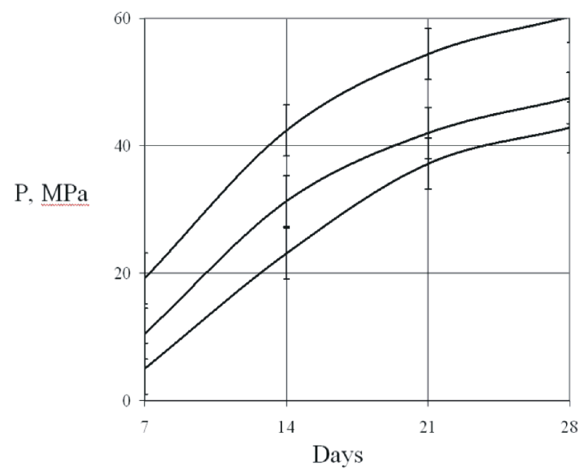
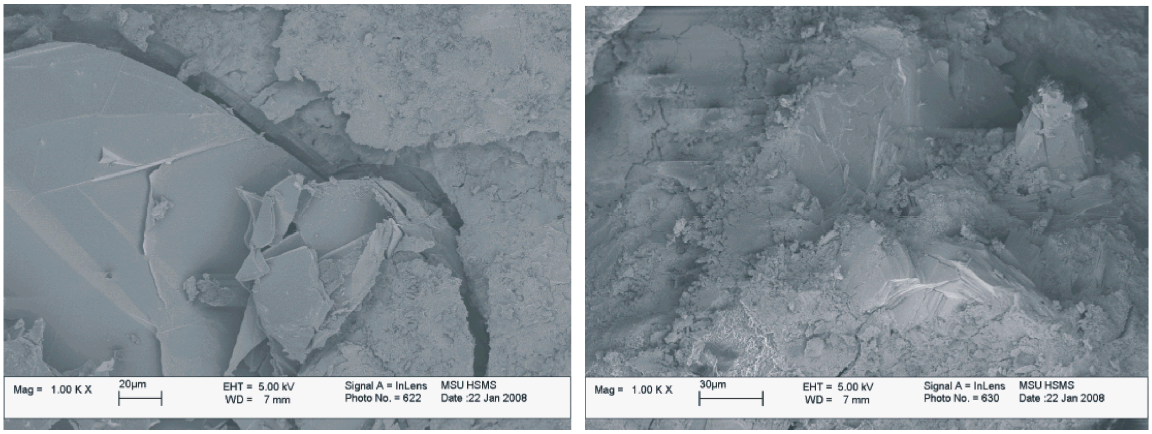


Fig. 5: The strength properties of cement systems: 1 - no addition; 2 - with the addition of graphite, 0.005 (wt), 3 - with the addition of carbon nanotubes, 0.005 (wt.)

lying parallel to each other. At this stage, the formation of primary aggregates, which do not make a special contribution to the growth of the resistivity of silicate composite materials.

Probably at a concentration of about 0.40 carbon nanotubes (by weight) formed a three-dimensional volume mesh of globular aggregates and further increase their concentration has little effect on the electrical characteristics of the cement stone – CNT: electrical conductivity varies in the range of 0.18 – 0.2 ohm^{-1}. m^{-1}.

Attention should be paid to the fact that small concentrations of carbon nanotubes leads to loss of strength characteristics electrically conductive silicate composites, Fig. 5.



(1) (2)

Fig. 6: Micrographs of cement systems:
1 - with the addition of graphite, 0.005%; 2 - with the addition of carbon nanotubes, 0.005%.

High aspect number, large Young's modulus makes them incompatible with no further modification for use as reinforcing components in a silicate composites. Rather weak bond between the carbon particles and silica matrix composite leads to the expulsion of CNT from it in the process of loading the composite. Due to small size (20 – 200 nm) nanotube are not centers crystallization aggregating, they constitute a single turn with low resistance contact that reduces the overall strength.

The micrographs of cement systems show particulary this effect, Fig. 6. Visually we can determine that the fracture surface of cement with the addition of carbon nanotubes appears more dense and uniform.

CONCLUSION

Thus, carbon nanotubes have abnormal properties compared to graphite electrical dependencies, due to the size and shape of the particle: small size influences on the primary aggregation and the elongated shape affects the "threshold" aggregation – the concentration of particles, which occurs when a substantial increase in electrical conductivity conductivity (secondary aggregation).

Conclusions:

- It is shown that the electrical conductivity of the dispersion of graphite and carbon nanotubes in a heterogeneous system, based on cement determined by the degree of aggregation of particles.
- Carbon nanotubes have abnormal properties compared to graphite electrical dependencies due to the size and shape of the particles – the carbon nanotubes have more high electric conductivity values.
- Small size CNT affect primary aggregation and the elongated shape affects the critical particle concentration at which a significant increase in electrical conductivity – the electroconductive phases at concentrations of 0.15 – 0.3 (by weight), electrical conductivity of a heterogeneous system with CNT significantly higher than graphite.
- Small CNT concentration (0.005 – 0.007 wt.) is cause of reducing strength characteristics electrically conductive silicate composite materials compared with graphite.

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