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Influence of conditions for preparation of fullerene-containing carbon black on its microwave properties and yield of fullerenes

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Conditions for preparation of the fullerene-containing carbon black with the maximum yield of fullerenes were determined. A correlation between the dielectric constant of the carbon black in the microwave range and the yield of fullerenes was found. The relation of the fullerene-containing carbon black structure to the conditions of its preparation and dielectric constant are discussed.

Key words: fullerene-containing carbon black, fullerenes, dielectric constant.

Although works on fullerenes are numerous, studies of optimization of their yield are presently urgent. The experimental conditions of achievement of the maximum yield of fullerenes (~15%) depending on the parameters of arc process (*viz.*, inert gas pressure, arc current, inter-electrode distance, and chamber diameter) have been examined in detail.[1—4] Meanwhile, the properties of the fullerene-containing carbon black remain poorly studied so far. In particular, data on its microwave properties are lacking. The use of polar fullerene derivatives as microwave stuffs was only mentioned,[5] and the microwave properties of carbon nanosized tubes incorporated into the polymeric matrix were recently reported.[6]

In this work, the influence of the arc discharge parameters on the phase composition of the carbon black, its dielectric properties in the microwave region, and the content of fullerenes was studied.

Experimental

Fullerene-containing carbon black was prepared in a precision automated setup for electric arc graphite evaporation.[7] Samples deposited on the walls of the arc discharge chamber

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were used. They were studied both in the initial state and after extraction. Fullerenes (mainly C_{60} and C_{70}) were extracted with toluene in a Sohxlet apparatus for 18 h, and the extract was dried *in vacuo* at 250 °C. The yield of fullerenes was determined by weighing with an accuracy of 6—8%. The dielectric properties of the samples were measured on a radiophysical bench[8] at frequencies of 4.76, 2.73, and 1.66 GHz. Powders were placed in calibrated glass tubes 1.1—2.5 mm in diameter. The measurement accuracies of the real (ε′) and imaginary (ε″) components of the dielectric constant (DC) were 5 and 10%, respectively. The density of samples (bulk and in a glass tube) was measured by the weight method. Thermogravimetric (TG) analysis was performed on a Q-1000 derivatograph in the 20—1000 °C temperature interval with a heating rate of 20 °C min^{-1}.[9] Electron micrographs were obtained on a Philips EM-430ST transmission electron microscope at a voltage of 200—250 kV. Samples were prepared by the ultrasonic dispersion of the carbon black in acetone followed by the deposition of a droplet of the suspension on the carbon film placed on the Cu grid. The content of amorphous carbon and graphite structures and particles sizes were determined from the electron microscopic (EM) data. The size distribution of particles was determined using a CAPA-500 centrifugal (CF) analyzer (HORIBA, Kyoto, Japan) by the dispersion sedimentation method in the liquid phase. Particles were analyzed by light transmission. The carbon black powder was placed in a cell containing distilled water. The mixture was shaken for 30 s, then the cell with the suspension was placed in a centrifuge, and measurements were performed. The specific surface and specific volume of carbon pores were measured by the BET method.[10] All measurements (except EM) were performed for the same series of samples.

Results and Discussion

The most critical arc parameters affecting the composition of the products formed in the arc discharge are the velocity of conveying of the electrodes (V) and the gap width between them (L). The latter is nearly inverse proportional to V when the power of arc burning is maintained constant. A typical plot of the yield of fullerenes (Y) *vs.* electrode velocity at a helium pressure in the chamber of 66700 N m^{-2}, an anode diameter of 6 mm, and a current of 100 A is presented in Fig. 1.

This plot can conventionally be divided into three regions: I, region with a slow electrode conveying ($V < 3$ mm min^{-1}) in which the yield of fullerenes increases with an increase in V; III, region of fast electrode conveying ($V > 4$ mm min^{-1}) in which the yield of fullerenes decreases with V increase; and II, region in which $V \approx 3$ mm min^{-1} and a gap width of ~3.5 mm are optimum to obtain the maximum yield of fullerenes at the fixed helium pressure and arc current. With the helium pressure increase, region II shifts toward low electrode velocities and region I gradually disappears because the arc burning is unstable. For example, to achieve the maximum yield of fullerenes at a helium pressure of 267000 N m^{-2}, the electrode velocity should be decreased

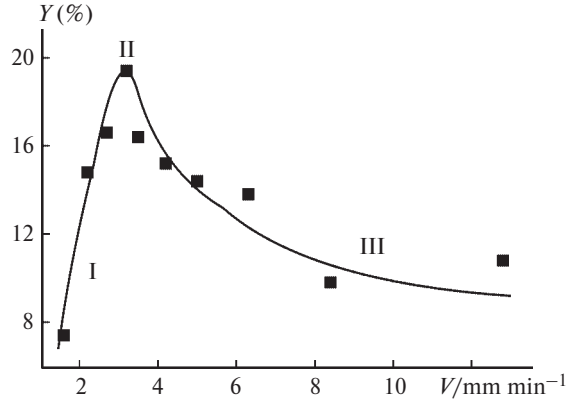

Fig. 1. Plot of the yield of fullerenes (Y) *vs.* electrode velocity (V).

to ~1.8 mm min^{-1} and the gap between the electrodes should be increased to a ~7 mm. A stable yield of fullerenes of ~20% (in some experiments, to 23%) is observed when V and L are optimum.

The DC values of the starting carbon black change, on the average, depending on the electrode velocity, from ~1.3 to ~2.1 for ε′ and from ~0.2 to ~0.4 for ε″, increasing on going from region I to region III. After fullerenes were extracted from the carbon black, these values increase by 3—4 times along with a great scattering of the DC values (≥50%) due to the different bulk densities of the samples in glass tubes. When the obtained DC values were normalized to the sample densities, we obtained a pronounced minimum in the region of the maximum fullerene yield in the curve of the normalized DC change.

The experimental plots of the real and imaginary parts of the normalized DC values of the starting carbon black measured at 4.76 GHz are shown in Fig. 2. It is surpris-

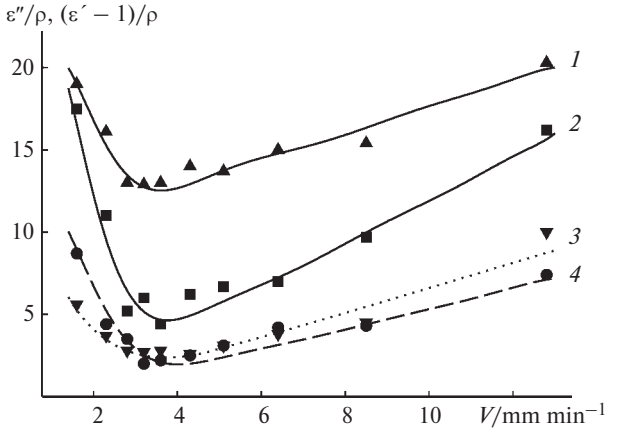

Fig. 2. Plots of (ε′ − 1) (*1*, *2*) and ε″ (*3*, *4*) normalized to the densities of the samples ρ (g cm^{-3}) *vs.* velocity of electrode conveying (V) for the carbon black extracted from fullerenes (*1*, *3*) and starting carbon black (*2*, *4*). The frequency was 4.76 GHz.

Table 1. Main characteristics of fullerene-containing carbon black samples

Characteristics	Value*		
	I	II	III
Fraction of amorphous carbon (EM) (%)	—	60—70	40—50
Fraction of graphite structures (EM) (%)	—	~10	~50
Fraction of amorphous carbon (TG) (%)	94—100	70—80	73—80
Fraction of graphite structures (TG) (%)	6	20—30	20—22
Specific surface /$m^2\ kg^{-1}$	260000	150000	200000
Specific pore volume /$m^3\ kg^{-1}$	—	$11 \cdot 10^{-5}$	$9.4 \cdot 10^{-5}$
Effective sizes of particles (μm) and their distribution (CF)**	>10 (~30), 1—10 (~65), <1 (~5)	>1 (~5), 0.4—1 (~60), <0.4 (~35)	>1 (~25), 0.4—1 (~35), <0.4 (~40)

* The data correspond to the velocities V = 1.6, 3.2, and 12.8 mm min^{-1}, which most adequately characterize regions I—III in Fig. 1.
** In parentheses.

ing that the observed deep minimum of the normalized DC (2—4-fold decrease relatively to the sides) in region II is not associated with a high concentration of fullerenes because this minimum is retained when they are removed from the powder. Similar results were obtained at 1.66 and 2.73 GHz.

In order to explain the plots of the fullerene yield and DC change *vs.* electrode velocity for the samples studied, we performed additional studies: TG measurements, determination of the size distribution of the carbon black particles using a centrifuge, and measurements of the specific surface and specific volume of pores. The results are presented in Table 1.

The data obtained allow the following conclusions. 1. In region I the content of amorphous carbon is >90%, in region II it decreases to ~70%, and in region III it either remains almost the same (TG data) or decreases further by 20% (EM data). 2. The content of graphite structures in region I is minimum; it increases to ~20% in region II and either virtually retains its value in region II (TG data) or continues increasing (EM data). 3. The size distributions of the carbon black particles in three regions are different. In region I the particles with a size of 1—60 μm predominate, whereas in regions II and III, the particles <1 μm in size prevail. At the same time, in region III the fraction of particles with a size of 1—70 μm increases. Note that the particles obtained in regions I and II are water-wettable, whereas in region III up to ~30% (by weight) particles are water-unwettable. 4. In region II the specific surface of the carbon black decreases, while the pore volume remains virtually unchanged.

The presence of fullerenes, the properties of the amorphous and crystalline components of the carbon black, and the size distribution of the particles cannot be responsible for a minimum on the normalized DC curve in region II. Although the particles differ in sizes in three regions, they are too small to have an effect on the DC change.[11] It is most likely that a more important factor is the formation of agglomerates with different conducting chain structures in the carbon black powder similarly to those in the industrial carbon black.[12] The data in Table 1 show that precisely the parameters that determine the carbon black structural rearrangements (*viz.*, sizes of particles and pores and specific surface) and the formation of conducting chain structures undergo changes in region II. This is also indicated by the disappearance of the DC minimum when the particles are wetted with Nujol, which violates the conductivity in the chain structure.

Changes in sizes of the carbon black particles, in pore sizes, and in the relative content of amorphous and crystalline carbon with changes in the V and L parameters produce, most likely, the structural rearrangement of the carbon black, changes its conducting and dielectric properties, and cause the correlation observed between the yield of fullerenes and DC.

Thus, the use of the electrode velocity and gap width corresponding to region II provides the optimum conditions for the formation of both atomic carbon and small clusters, which results in the maximum yield of fullerenes. The experimental yield of fullerenes depends, as shown in the theoretical work,[13] on the conditions of carbon vapor condensation, which are determined by the characteristics of mixing of the vapor with an inert atmosphere in the radial-slit turbulent stream.

The retention of minima of the normalized DC components after fullerenes removing from the starting carbon black (see Fig. 2) indicates that the observed DC minimum is not related to the presence of fullerenes but is explained, most likely, by the formation of a new carbon black structure, which is not decomposed after fullerene extraction. Perhaps, the formation of fullerenes and the new carbon black structure are mutually related processes.

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References

1. D. V. Afanas´ev, I. O. Blinov, A. A. Bogdanov, G. A. Dyuzhev, V. I. Karataev, and A. A. Kruglikov, *Zh. Teor. Fiz.* [*Russ. J. Theor. Phys.*], 1994, **64**, No. 10, 76 (in Russian).
2. D. V. Afanas´ev, A. A. Bogdanov, G. A. Dyuzhev, and A. A. Kruglikov, *Zh. Teor. Fiz.* [*Russ. J. Theor. Phys.*], 1997, **67**, No. 2, 125 (in Russian).
3. O. A. Nerushev and G. I. Sukhinin, *Zh. Teor. Fiz.* [*Russ. J. Theor. Phys.*], 1997, **67**, No. 2, 41 (in Russian).
4. G. von Helden, M.-T. Hsu, N. Gotts, and M. T. Bowers, *J. Phys. Chem.*, 1993, **97**, 8182.
5. US Pat. 5317058; *Chem. Abstrs.*, 1994, **121**, 1033.
6. C. A. Grimes, C. Mungle, D. Kouzoudis, S. Fang, and P. C. Ekiund, *Chem. Phys. Lett.*, 2000, 319; 460.
7. A. Moravsky, P. Fursikov, and A. Ryabenko, in *Abstr. Book of 189th Meeting of the Electrochemical Society, Fullerenes S1*, Los Angeles, 1996, 112.
8. V. S. Savost´yanov, V. N. Vasilets, O. E. Ermakov, E. A. Sokolov, D. A. Kritskaya, A. D. Pomogailo, and A. N. Ponomarev, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2073 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1615 (Engl. Transl.)].
9. L. G. Berg, *Vvedenie v termogravimetriyu* [*Introduction into Thermogravimetry*], Nauka, Moscow, 1969, 395 pp. (in Russian).
10. S. Lowell and J. E. Shiellos, *Powder Surface Area and Porosity*, Chapmann and Hall, London—New York, 1984.
11. L. Levin, *Teoriya volnovodov* [*Waveguide Theory*], Radio i Svyaz´, Moscow, 1981, 311 pp. (in Russian).
12. P. G. Filippov, V. G. Shevchenko, A. T. Ponomarenko, V. A. Benderskii, and A. A. Ovchinnikov, *Elektricheskie svoistva polimernykh kompozitov s elektroprovodyashchimi dispersnymi i voloknistymi napolnitelyami* [*Electrical Properties of Polymeric Composites with Electroconducting Properties Dispersed and Fibrous Stuffs*], NIITEKhIM, Moscow, 1984, 56 pp. (in Russian).
13. A. V. Krestinin and A. P. Moravsky, *Chem. Phys. Lett.*, 1998, **286**, 479.

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