Structure and phase composition of electrically conductive carbon black

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Abstract. A comprehensive study of the structure and phase composition of a promising brand of electrically conductive carbon black was carried out. It is shown that the material under study has a complex phase composition, which, along with carbon, includes other elements and compounds, such as sulphur, oxygen, nitrogen, and vanadium oxides. The structural state of carbon black can be defined as amorphous. The presence of functional oxygen-containing groups in the material, presumably attached to the edge carbon atoms of graphene layers, has been proved. The interrelation of some characteristics of the structure and phase composition of the material and the properties of polymer composites is discussed.

Keywords: electrically conductive carbon black, structure, phase composition, chemical composition

1. Introduction

Electrically conductive polymer composite materials (composites) are used in various fields of industry: space, petrochemical, medical industries and mechanical engineering. Widespread use of such composites is resulted from their unique properties in their combination. The conductivity of composites is ensured by the use of electrically conductive, most often carbon fillers. The filler forms a conductive structure in the matrix, varying the parameters of which it is possible to obtain materials with a given level of antistatic, electrically conductive, shielding characteristics. One of the promising fillers for electrically conductive polymer composites is carbon black (CB) [1-5].

In this case, the choice of the filler that is adequate to the problem being solved is important, the characteristics of which largely determine the electro-physical properties of the composite. Among such characteristics, the phase composition of the filler, its dispersion, electrical conductivity, other physical and chemical parameters, as well as such characteristics of its surface as the energy of the thermodynamically stable conformation of the surface carbon layer, the presence of functional oxygen-containing groups on the surface are usually considered [6-7]). Correct and comprehensive accounting of these and other factors within the framework of a systematic materials approach to the formation of predetermined properties of materials and the rational choice of fillers and matrix is a difficult task.

Currently, the developments of electrically conductive composites is mainly based on very limited empirical data in terms of volume and degree of generalization and, sometimes, without taking into account the mechanisms determining the relationship between the structure and physical properties of
materials in the process of their manufacture and operation. Thus, a comprehensive study of the structure, phase composition and properties of promising grades of carbon black is a necessary step in solving the materials engineering problem of developing composites with predetermined properties.

2. Objects and methods of research

The structure and phase composition of highly dispersed electrically conductive carbon black of the OMCARB C140 brand, Technical Data Sheet OMCARB No. Omsk-07-2014 Revision 2 of 28-07-2014 [5] (produced by Omsk Carbon Group), which is used in the production of electrically conductive plastics, antistatic rubbers, and anode rubber grounds, were studied in this work. Carbon black C140 is obtained during the furnace process. CB globules are characterized by low density, the particle size being 20-56 nm [6]. The main physical and chemical parameters of this CB brand are given in publications [8, 9]. However, to date, there are no systematic data on the structure and phase composition of this CB brand, which would allow us to form a comprehensive idea of the relationship of these parameters with the properties of composites, the possibilities of modifying the surface of filler particles and thus increase the efficiency of using TU of the C140 brand when creating polymer composite materials.

X-ray studies of the CB were carried out using XRD-7000 diffractometer (Shimadzu) using CuKa radiation (\(\lambda = 1.54 \text{ Å}\)). Scan range \(2\theta = 10^\circ \ldots 70^\circ\). The estimation of the depth of the surface layer that reduces the intensity of X-ray radiation by half, using the value of the mass attenuation coefficient of radiation [10], took a value of about 4 mm.

Scanning electron microscopy and elemental analysis of CB were carried out using a JCM-5700 (JEOL) microscope equipped with a JED-2300 X-ray energy dispersion spectrometer (JEOL). The maximum electron path length in a substance, calculated using the Kanaya-Okayama model [11], was approximately 28 microns.

X-ray photoelectron spectroscopy (XPS) was performed at the Surface Science Center (Riber) unit. The energy resolution of the spectrometer when registering the spectra of the core levels assumed a value of about 0.2 eV, when registering the survey spectra - about 1 eV. Non-monochromatic Al K\(\alpha\) radiation (\(E = 1486.6 \text{ eV}\)) was used to excite the XPS spectra. The diameter of the X-ray beam was approximately 3 mm. The thickness of the analysed layer of the substance was approximately 3 nm. The spectra were measured in an ultrahigh vacuum of \(1 \times 10^{-8} \text{ Torr}\). The thickness of the analyzed layer of the substance was approximately 3 nm. When decomposing the spectra, the CASA XPS software package was used.

3. Experimental results and discussion

On the micrographs of the CB (Fig. 1, 2a), agglomerates of the studied material particles of various sizes (from 5 microns to 1 mm) and shapes with different degrees of looseness are identified. The sizes of CB agglomerates reach values exceeding the sizes of particles (globules) by three orders of magnitude. Depending on the degree of the initial agglomerates reduction and the degree of particles dispersion in the polymer matrix, the properties of the composite will differ significantly.
In the energy dispersion spectrum of CB (Fig. 2b, 3b), in addition to carbon, oxygen, lead, copper, sulphur, sodium, and vanadium are identified. In various samples, in different areas of the studied CB samples and at certain points, the mass content of oxygen is up to 10 %, lead - up to 2 %, copper - up to 1.7 %, sulphur - up to 1.1 %, sodium - up to 0.8 %, vanadium - up to 0.4 %. The presence of elements other than carbon is associated with the peculiarities of the material production technology (presumably the presence of sulphur, carbon and sodium), as well as possible artifacts introduced into the material during its transportation and storage.

Figure 1. Micrographs of CB, magnification ×300 and ×500 times

Figure 2. Micrography (a) and the energy dispersion spectrum (b) of the CB identified on the surface area
Figure 3. Micrography (a) and the energy dispersion spectrum (b) of the CB identified at the point.

The diffractogram of the CB sample obtained using an X-ray diffractometer is shown in fig. 4.

Two blurred reflexes characteristic of carbon are distinguished on the diffractogram (reflex 002 with a maximum of $2\theta = 24.8^\circ$ and reflex $10l$ (overlap of reflexes $100$ and $10l$) with a maximum of $2\theta = 43.8^\circ$). The reflexes identified on the diffraction pattern for angles $2\theta$ equal to $37.8^\circ$; $44.1^\circ$; $64.4^\circ$ respectively, do not belong to crystalline carbon.

The diffractogram was used to determine the main X-ray structural characteristics of carbon using a well-known technique used, for example, in [13]. The interplane distance calculated for the 002 reflex according to the Wolf-Bragg formula is $d_{002} = 3.59 \text{ Å}$, which is close to the data given in [14] for CB UM66, UM76, and UM85. The size of the coherent-scattering regions (CSR) responsible for diffraction effects in the direction perpendicular to the graphene layers ($L_c$) and the regions responsible
for diffraction effects in the direction along the graphene layers \((L_a)\) were determined using the formulas [15]:

\[
L_c = \frac{0.89\lambda}{(\beta \cos \theta)},
\]

\[
L_a = \frac{1.04\lambda}{(\beta \cos \theta)},
\]

where \(\lambda\) is the wavelength of the X-ray radiation; \(\beta\) is the corresponding half-width of the diffraction maximum minus the instrumental broadening (a silicon diffractogram was used in the calculations); \(\theta\) is the corresponding Bragg angle. When calculating the value of \(L_c\), the reflex 002 was used, when calculating \(L_a\), the reflex 10\(l\) was used.

The calculated values of the OCD dimensions are: \(L_c = 14.6\) Å; \(L_a = 39.8\) Å. The value of \(L_c\) corresponds to the data given in [14] for CB brands UM66, UM76, and UM85.

The degree of CB crystallinity was calculated based on a diffractogram using the technique proposed by the authors of [16], as the ratio of the crystallinity index of the sample under study to the crystallinity index of the standard (in this study, silicon):

\[
X = \frac{IC}{IC_e} \times 100\%,
\]

where \(IC\) is the crystallinity index of the test sample (deg\(^{-1}\)); \(IC_e\) is the crystallinity index of the standard (grad\(^{-1}\)).

The crystallinity index was calculated as the ratio of the modulus integral of the intensity derivative over angle 2\(\theta\) to the intensity integral over angle 2\(\theta\) [16]:

\[
IC = \frac{\int_{\beta}^{a} \int_{2\theta = a}^{b} |dI| d\theta d\theta}{\int_{2\theta = a}^{b} I d\theta d\theta},
\]

where \(IC\) is the crystallinity index (deg\(^{-1}\)), \(a \ldots b\) is the scanning range by angle 2\(\theta\), \(I\) is the intensity.

The calculated value of CB crystallinity degree is equal to \(X = 1.4\%\).

The blurring of the 002 and 10\(l\) reflexes, the small size of the CSR and the low value of crystallinity degree indicate the small size and content of clusters consisting of ordered graphene layers in carbon, as well as a strong distortion of interatomic distances. The structural state of carbon black can be defined as amorphous.

The panoramic XPS spectrum of a carbon black sample is shown in Fig. 5, the results of quantitative analysis carried out on the panoramic spectrum using the method of elemental sensitivity coefficients are presented in Table 1.

In the panoramic XPS spectrum of the sample, there are lines of carbon C 1s (binding energy is about 285 eV), oxygen O 1s (binding energy ~ 530 eV), the auger transition line of oxygen O KLL (binding energy is about 970 eV). There are also low-intensity vanadium V 2p (binding energy is about 517 eV) and nitrogen N 1s lines (binding energy is about 400 eV).
Figure 5. Panoramic XPS spectrum of a carbon black sample

Table 1. Composition of the surface of the samples according to the XPS data

|       | Concentration, at. % |
|-------|----------------------|
| [C]   | 97.0                 |
| [O]   | 2.4                  |
| [V]   | 0.3                  |
| [N]   | 0.3                  |

Vanadium line on the spectrum is asymmetric and very noisy due to the low concentration of this element (Fig. 6). Based on the publications [17-19] and the XPS data, it can be assumed that a mixture of vanadium oxides, including V$_2$O$_5$ and VO, is present in the material. The presence of VO is confirmed by the identification of reflexes for angles 2$\theta$, equal to 37.8°; 44.1°; 64.4°, on the diffractogram of the CB sample (Fig. 4).

Figure 6. XPS spectrum of oxygen O 1s lines and vanadium doublet line V 2p.
The lines of sulphur, as well as some other elements (lead, copper, sodium) present in the sample according to energy dispersion analysis, are not observed in the XPS spectrum. This, presumably, can be explained by taking into account the different depth of energy dispersion methods analysis and XPS. Apparently, these elements are either deeper than the surface layer that is analysed in the XPS, or they are concentrated in the space between the agglomerates of particles of the studied material and are distributed very unevenly. In addition, the coefficient of elemental sensitivity in the XPS for vanadium is 1.4, which is more than 3 times higher than, for example, for sulphur (0.35).

The presence of a small amount of nitrogen in the surface layer of the sample is probably due to its adsorption during storage of the sample in air (Table 1). A certain proportion of oxygen is also in the adsorbed form (Table 1). The other part of oxygen is found in the composition of vanadium oxides, as well as in the form of various functional oxygen-containing groups attached to the edge carbon atoms of graphene layers (Fig. 7). The presence of such groups leads to the defectiveness of graphene layers, changing the energy of the thermodynamically stable conformation of the surface carbon layer and creating conditions for increasing the density of the elastomeric matrix in the interfacial layer, thereby increasing the gas barrier properties of the polymer composite, as shown in [7].

![XPS spectrum of the carbon C 1s line.](image)

**Figure 7.** XPS spectrum of the carbon C 1s line.

4. **Conclusion**

The main characteristics of the structure and phase composition of electrically conductive carbon black are determined. It is established that the structure of the material under study is characterized by small CSR sizes and a low value of crystallinity degree, which indicates the small size and content of clusters consisting of ordered graphene layers in carbon, a strong distortion of inter-atomic distances. The structural state of carbon black can be defined as amorphous. The material under study has a complex phase composition, which, along with carbon, includes other elements and compounds, such as sulphur, oxygen, nitrogen, and vanadium oxides. The structural state of carbon black can be defined as amorphous. The presence of functional oxygen-containing groups in the material, presumably attached to the edge carbon atoms of graphene layers, has been found out.

5. **Acknowledgement**

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