Porous structure of carbon-based materials studied by means of X-ray small angle scattering method

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The porous structure of carbon-graphite materials: styrene-divinylbenzene copolymer (SBC) and fruit stones (FS) has been studied by means of X-ray small angle scattering method. The angular dependences of scattered intensities have been obtained and analyzed by means of the Guinier method. The main parameters of porous structure have been determined (inertia radius, pore size distribution functions, specific surface areas).

Keywords: nanoporous carbon, porous structure, specific area, X-ray small angle scattering.

1. Introduction

Porous materials are widely used in various areas of application. One such group in the carbon-graphite porous materials whose main characteristics are interesting for electronics and engineering. For instance, a high degree of nanoporosity (40–45%) at total porosity (70–75%) allowed them to be considered as promising materials for use in modern electric engineering (molecular energy storage, supercapacitors, galvanic batteries, *etc*.) [1, 2]. Besides, introducing various kinds of filling agents permits varying the physical-chemical properties of such nanocomposites within a wide range [3].

In order to control the technological process and improve the properties of carbon-graphite nanocomposites detailed studies, including structural ones, are needed. Though being poor, the available literature data indicate that nanoporous carbon-graphite materials show some unique characteristics: narrow pore size distribution (6–40 Å), large specific surface area (600–1500 m^2/g) and sorbtion capacity (from 0.5 up to 0.73 sm^3/sm^2) [4, 5].

Therefore, it is of great importance that the main parameters of porous structure in carbon-graphite materials be studied. The small angle X-ray diffraction is widely used for studying the structure of nanoscale materials of different kind. In this paper, we

use this method in order to obtain the parameters of porous structure for two carbon materials: styrene-dyvinilbenzene copolymer (SBC) and fruit stones (FS).

2. Experimental

Experimental studies of porous structure were carried out with the use of DRON-3 diffractometer attached to a special focusing system. Cu Kα-radiation ($\lambda = 1.5418$ Å) was monochromatized by means of reflecting from planes (111) of perfect Ge single crystal in transmitting regime. The thickness of samples under investigation was 1 mm. The slit system allowing ± 4 mm displacement perpendicular to X-ray beam direction was used in order to cut down the parasite scattering from monochromator and reduce noise before specimen and detector. Using a perfect Ge crystal and precisive focusing system allowed us to measure the small angle spectrum starting from a 0.01 Å^{-1} wave vector. For better resolution ($\Delta 2\theta = 0.03°$) a 0.1 mm slit was installed before the detector. The scattered intensities were recorded in scanning regime within 0.25–4.0° range with 0.05° step and 100 s exposition.

3. Results and discussion

The X-ray small angle spectra for materials under investigation are shown in Fig. 1**a**. Similar behaviour is observed for both kinds of materials. The scattered intensity curves fall down gradually over the entire angle range indicating the random distribution of scattering inhomogeneities (pores). The intensity curves obtained were analyzed based on the Guinier approach [6]. According to the Guinier formula the intensity of X-ray small angle scattering for monodispersed system is:

$$I(s) \; = \; I(0)\exp\left(-\frac{1}{3}s^2 \text{Rg}^2\right) \tag{1}$$

where Rg – electronic inertia radius, which is the characteristic of the electron density fluctuation scale; $I(0)$ – scattered intensity at $s = 0$ which depends on the total quantity of scattered substance. In logarithmic coordinates formula (1) can be written:

$$\ln\left[I(s)\right] \; = \; \ln\left[I(0)\right] - \frac{1}{3}s^2 \text{Rg}^2 \tag{2}$$

Commonly, the dependence $\ln\left[I(s)\right] = f(s^2)$ shows the linear behaviour for monodispersed systems. For samples under investigation this dependence (Fig. 1**b**) significantly reveals nonlinear behaviour, which is typical of polydispersed systems with wide pore size distribution. In this case, the scattered intensity can be written as the sum of partial intensities, each of them corresponding to the scattering from pores of some definite size:

$$I(s) \; = \; \sum_k I_k(0)\exp\left(-\frac{1}{3}s^2 \text{Rg}_k^2\right) \tag{3}$$
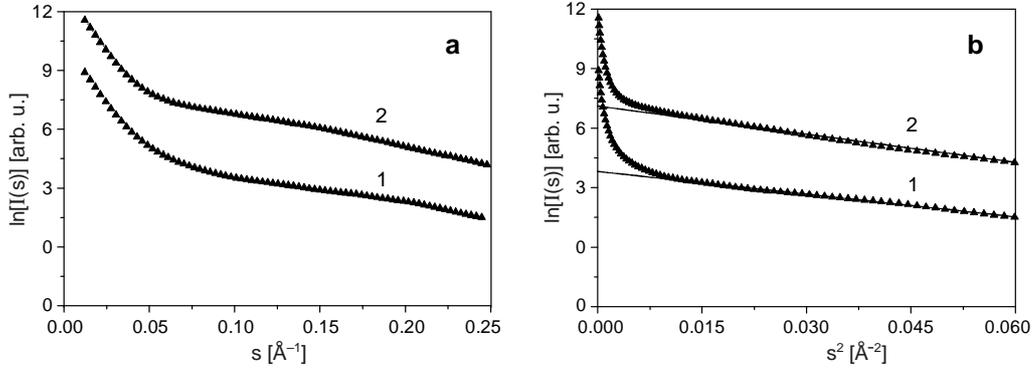
Fig. 1. Small angle scattering curves for SBS (1) and FS (2) materials $\ln[I(s)]-s$ coordinates (**a**) and $\ln[I(s)]-s^2$ coordinates (**b**).

In order to analyze the obtained results the tangent method [7] was used. Within a 0.08–0.25 Å^{-1} wave vector region $\ln[I(s)] = f(s^2)$ curves can be extrapolated by linear functions. The slope of the lines allowed us to determine the size of the least porous fraction Rg_1, whereas the ordinate of the point at which this line crosses $\ln[I(s)]$ axis is the $I_1(0)$ value. The drastic increase of scattered intensity at small angles is caused by the existence of large scale inhomogeneities in materials under investigation. Formula (1) permits us to determine the contribution of the least size pores to the total scattered intensity:

$$I_1(s) \;=\; I_1(0)\exp\!\left(-\frac{1}{3}\,s^2\,Rg_1^2\right) \tag{4}$$

In a similar way, one can obtain Rg_k and $I_k(0)$ for each porous fraction. The obtained parameters of intensity curve are used for calculation of volume portion of each porous fraction:

$$m_k \;=\; \frac{I_k(0)}{Rg_k^3}\;\frac{1}{\displaystyle\sum_k \frac{I_k(0)}{Rg_k^3}} \tag{5}$$

In Figure 2**a**, distribution functions of scattered centers are shown with respect to inertia radius for SBC and FS calculated in Gauss approximation according to a formula proposed in [3]. The calculation was based on the assumption that the scattering of pore size around the mean value (dispersion) $\Delta Rg_k \approx Rg_k$ satisfies the equation:

$$F(Rg) \;=\; \frac{2}{\sqrt{\pi}}\sum_k \frac{m_k}{\sqrt{Rg_k}}\exp\!\left[-\frac{(Rg - Rg_k)^2}{Rg_k^2}\right] \tag{6}$$
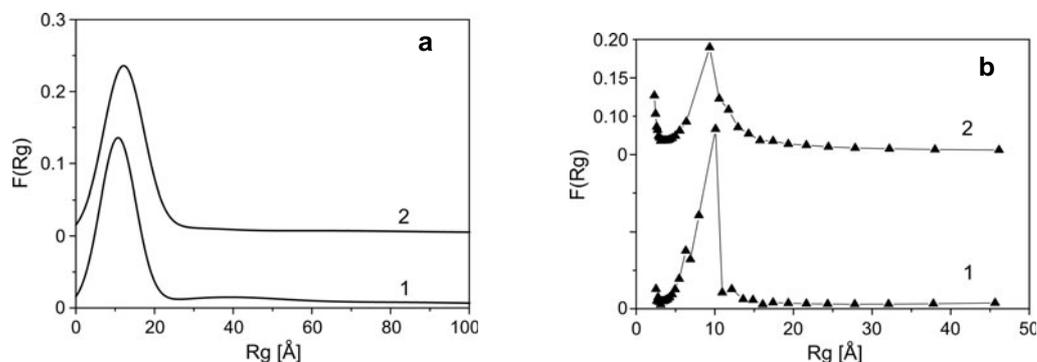
Fig. 2. Pore size distribution function for SBC (curve 1) and FS (curve 2).

As can be seen from the results obtained, the main contribution into porous structure of SBC and FS is due to the nanoporous ones with mean inertia radii of 10.5 Å and 12.0 Å, respectively.

Pore size distribution functions, calculated from the small angle X-ray scattering are compared with ones obtained by means of precisive porometry (Fig. 2**b**). As can be seen, there is an agreement between maxima positions for both curves, which confirms similarity of the most probable size values of the pores. Besides, the analysis of distribution functions, obtained by means of porometry, allowed us to estimate the total specific pore surface value of 1044 m^2/g for SBC and 453 m^2/g for FS, showing correlation with data obtained by means of the small angle scattering (see the Table).

Another principal characteristic of porous structure that allows us to determine the absorption properties of nanocarbon materials is the specific porous surface area, which can be approximately calculated using the small angle scattering data. For calculation of the specific porous surface area of k-fraction the following equation can be used:

$$S_k = \frac{s_k N_k}{\rho_m V} \tag{7}$$

T a b l e. Porous structure parameters for SBS and FS.

	Rg_k [Å]	m_k	S_k [m^2/g]	V_k [sm^3/g]
SBS	10.5	0.660	1086	0.49
	35.0	0.107	52	0.08
	75.0	0.116	28	0.09
	135.0	0.117	15	0.09
FS	12.0	0.744	557	0.39
	25.0	0.053	18	0.03
	55.0	0.070	11	0.04
	110.0	0.133	11	0.07

where V – scattering volume, s_k – surface area for k-fraction pores, N_k – number of k-fraction pores, ρ_m – density of porous carbon.

Let us introduce a porosity coefficient expressed as the ratio of pore volume to the total volume:

$$\alpha = \sum_k \frac{\upsilon_k N_k}{V} \tag{8}$$

where υ_k – pores volume of k-fraction. Formula (7) can be rewritten:

$$S_k = \frac{s_k N_k}{\rho_m \sum_k \upsilon_k N_k} \tag{9}$$

For spherically-shaped pores one can write:

$$S_k \approx \frac{3\,\alpha\, m_k}{\rho_m \mathrm{Rg}_k} \tag{10}$$

where m_k – volume fraction of k-fraction pores.

In a similar way, one can obtain the formula for specific porous volume:

$$V_k \approx \frac{\alpha}{\rho_m} m_k \tag{11}$$

The integral porosity coefficient can be estimated by means of a method presented in detail in [8]. According to the formalism of this method one can write:

$$\alpha = 1 - \frac{\rho_m}{\rho_x} \tag{12}$$

where ρ_x – X-ray density for amorphous carbon. Hydrostatic weighing yields the following values: $\rho_m = 0.8$ g/sm^3 (SBC) and $\rho_m = 1.0$ g/sm^3 (FS).

In order to determine ρ_x we have obtained the diffraction spectra for SBC and FS within a wider interval of scattering angles (Fig. 3). Besides, the X-ray diffraction investigation of high purity graphite was carried out, too. The Breg formula was used to calculate the $d_{(002)}$ interplanar distance for graphite:

$$d_{(002)} = \frac{\lambda}{2\sin(\vartheta)} \tag{13}$$

In [8], it was found that X-ray density for amorphous coal equals:

$$\rho_x = \frac{d_{(002)}}{d_x} \rho_c \tag{14}$$

where $\rho_c = 2.26$ g/sm^3 – graphite density, $d_x = 6.28/s_1$, s_1 – position of peak in diffusive "halo" in diffraction pattern for amorphous carbon. It is found that X-ray
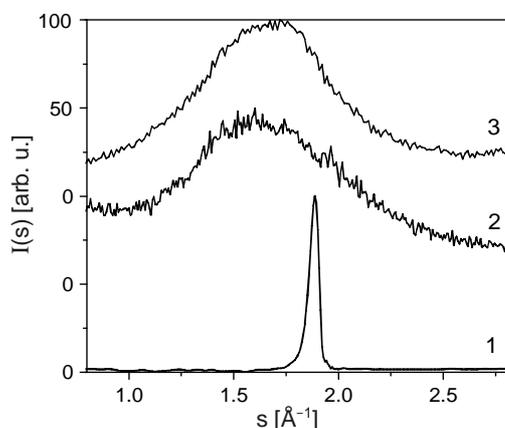
Fig. 3. X-ray diffraction patterns (1 – high purity graphite, 2 – SBC, 3 – FS).

density for SBC and FS equals $\rho_x = 2.0$ g/sm^3. Consequently, the integral porosity coefficients equal 59.5% and 51.0% for SBC end FS, respectively. The results of calculation of the porous structure parameters for samples under investigation are listed in the Table. As can be seen, the SBC material is characterized by a better developed porous surface (1180 m^2/g) in comparison with that for FS (600 m^2/g), which is supposed to be caused by nanopores of size less by 1.15 factor in size.

4. Conclusions

Analysing the pore size distribution function obtained allowed us to conclude that the main contribution into the porous structure is due to nanopores with the mean inertia radius of 10.5 Å (SBC) and 12.0 Å (FS). The approximate relations for determination of specific porous surface and specific porous volume for polydispersed carbon materials are derived to be:

$$S \approx 3 \sum_k \frac{\alpha\, m_k}{\rho_m \mathrm{Rg}_k}$$

$$V \approx \sum_k \frac{\alpha\, m_k}{\rho_m}$$

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