

APPLICATION OF FRACTAL GEOMETRY FOR STUDIES OF HETEROGENEITY PROPERTIES OF NANOMATERIALS

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Calculations based on the fractal geometry in the estimation of surface heterogeneity are superior compared with conventional calculation methods (e.g. from the data of gas adsorption or X-ray radiation scattering) as they can be applied without limitation as far as the range of surface sizes of the studied structures is concerned. This paper presents structural characteristics of carbon and carbon-free nanomaterials based on the determined surface and volumetric fractal coefficients. Fractal coefficients were determined from the data obtained by means of two independent methods: sorptometry and atomic force microscopy (AFM). Correlation between porosity parameters and fractal coefficients is presented.

Keywords: atomic force microscope, fractal dimension, heterogeneity, nanomaterials, sorptometry

Introduction

Recently, unusual objects, fractals, have aroused great interest in scientists working on the border-line of physics and mathematics. Never before had a mathematical idea been accepted so rapidly and aroused such interest. Fractals were accepted so rapidly and aroused such interest. There are connecting links with dynamic systems, geometry, theory of numbers but fractal geometry is the extension of classical geometry and can be used for creating accurate models of physical structures.

Benoit Mandelbrot is regarded to be the father of fractal geometry. However, many fractals and their descriptions originate from classical mathematics. The mathematicians contributing to the development of fractal theory are: George Cantor, Giuseppe Peano, David Hilbert, Helg von Koch, Waclaw Sierpinski, and Felix Hausdorff. The word 'fractal', introduced into scientific terminology by Mandelbrot, comes from the Latin word *fractus*-broken. Mandelbrot assumed that Euclidean geometry is not suitable for description of nature-mountains are not cones and the coastline is not a segment. These are rather shapeless forms that are fractals. They are characterized by great self-resemblance, each fragment resembles the whole.

So far theoretical and experimental works on application of fractal geometry for structural characterization of solids of a complex structure have been successful [1–4]. The condition they must satisfy is self-resem-

blance of the structure tending towards infinity in size reduction. Nanomaterials, being the subject of study in this paper, satisfy this condition and can be identified with fractal objects. During the scaling process, heterogeneity of nanomaterial surfaces or layers forming them, do not change. Mathematical descriptions of the surface should reflect this property and be in agreement with the theoretical structural models.

Depending on the kind of solid surfaces, they can be defined as Euclidean, non-porous, completely flat surface S equal to the square of their linear dimension R [5]:

$$S_{\text{flat}} = R^2 \quad (1)$$

In the case of finite fluctuations within the completely flat surface, the range of effective surface is proportional to the linear square of dimension R and constant c :

$$S'_{\text{flat}} = R^2 c \quad (2)$$

When fluctuations depend on the surface size, the effective surface extends within the third dimension. Then extension of surface is defined:

$$S_{\text{fractal}} = R^{D_f} c \quad (3)$$

where $3 \geq D_f > 2$ is fractal dimension.

This paper presents application of calculated fractal coefficients for characterization of geometrical heterogeneity properties of chosen nanomaterials.

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Experimental

Material and apparatus

Carbon nanomaterials i.e. single and multiwall nanotubes, fullerenes (D1, B1, F1-6) produced by Sigma-Aldrich as well as commercial carbon nanotubes (N1, N2, N3) were prepared using the methods described in [6–8]. Moreover, carbon-free nanomaterials (C1 and C2) and molecular sieves (M1 and M2) were studied. The procedures for preparing the samples of molecular sieves, Na^+ [Si/Ti]MCM-41-X and Na^+ [Si/Al]MCM-41-X, where X is the ratio Si/Ti or Si/Al, have been described elsewhere [9, 10]. Carbon black (S1 and S2) comes from the rubber industry.

Table 1 presents properties of the studied materials, including their outer (O.D.) and inner (I.D.) diameters as well as length (l) of commercial carbon nanotubes, given by the producer. Specific surface areas (S_{BET}) as well as average pore diameters (D_{av}) of the studied materials were determined using sorptometry.

The data needed for calculation of fractal coefficients were obtained from the sorptometric measurements by means of a Sorptomat ASAP 2405 V1.01 (Micro-metrics Co., USA), and micrographs of the surfaces of studied nanomaterials were made by AFM Nano-Scope III type apparatus (Digital Instruments, USA).

Results and discussion

Calculations of fractal coefficients

Porous fractal coefficients determined from the sorptometric data

Fractal dimensions can have the following forms: porous, surface and mass [11]. The two first of these are

normally most frequently taken into consideration, including those of nanomaterials. From the sorptometric data the porous fractals, D_p , often called volumetric fractals, were calculated. For the object described by the porous fractal dimension, change of the pore volume, V_p , connected with the change of their radii, r_p , can be expressed by the equation:

$$dV_p/dr_p = K_p r_p^{2-D_p} \quad (4)$$

or

$$V_p \sim r_p^{3-D_p} \quad (5)$$

where K_p is a constant and D_p is porous fractal dimension.

The porous fractal dimension corresponds to irregularity in pore distribution. The values D_p are included in the range $2 < D_p < 3$. The higher the porous coefficient value, the greater is the distribution of pore sizes. A fractal coefficient equal to 2 corresponds to a material of homogeneous distribution of pores of almost equal size. The value close to 3 is assigned to the bodies of heterogeneous pore distribution.

The porous fractal coefficients were calculated from the isotherms of low-temperature nitrogen adsorption and desorption (presented in Fig. 1), using the methods based on the theories elaborated by Frenkel, Halsey and Hill as well as Kiselev from the following equations [12–18]:

$$D_f = 2 + n_f \quad (6)$$

$$D_f = 3 - d[\ln a(x)]/d[\ln(-\ln x)] \quad (7)$$

$$D_f = 2 + d[\ln(-\ln x) da]/d[\ln(-\ln x)] \quad (8)$$

where n_f is the fractional part of fractal, a is the size of adsorption and x is the segment of the experimental isotherm.

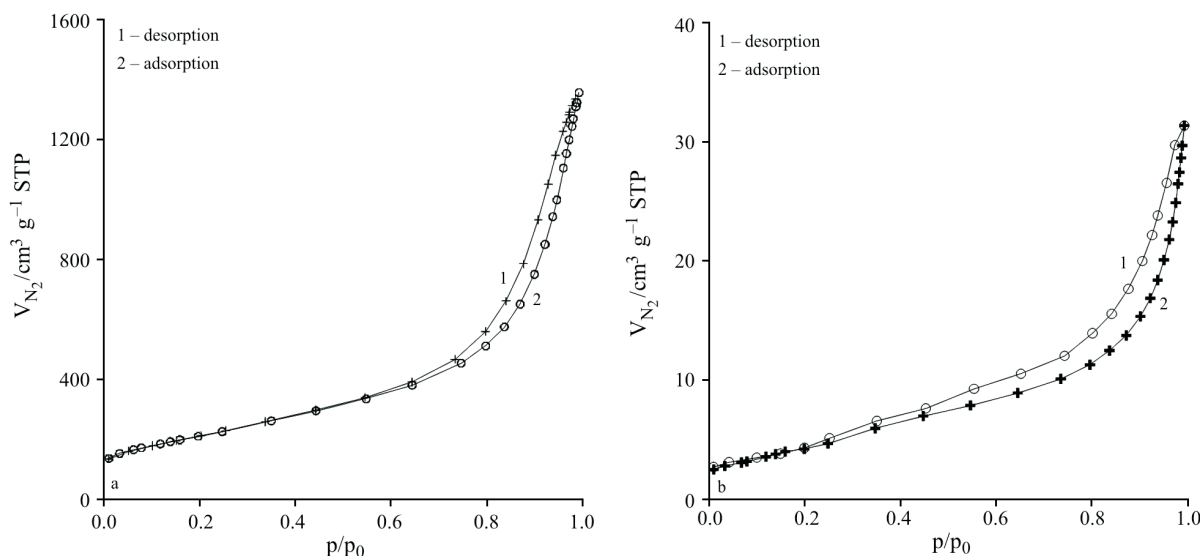


Fig. 1 Isotherms of nitrogen adsorption and desorption of the a – C1 and b – F5 samples

Table 1 Characteristics of some structural parameters of nanomaterials

Sample	Nanomaterials	O.D./nm	I.D./nm	$l/\mu\text{m}$	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	D_{av}/nm
D1	5,6 fullerene C_{70}				994.73	6.0
B1	carbon nanotubes single walled				280.90	8.97
B2	carbon nanotubes double-walled	1.3–5		50	742.85	10.57
F1	multiwall carbon nanotube	10–30	5–10	0.5–500	124.89	11.06
F2	multiwall carbon nanotubes	40–60	5–10	0.5–500	86.58	9.60
F3	MCN, powdered cylinder cores	2–15		1–10	32.05	15.8
F4	multiwall carbon nanotube	30–50	5–15	0.5–500	22.19	13.1
F5	MCN, cylinder cores shell removed				15.08	11.2
F6	MCN, as-produced cylinders	2–15		1–10	20.22	9.8
N1	multiwall carbon nanotubes				87.05	7.73
N2	multiwall carbon nanotubes				36.74	10.88
N3	multiwall carbon nanotubes				87.85	10.59
M1	Na^+ [Si/Ti] MCM-41-40				911.08	4.2
M2	Na^+ [Si/Al] MCM-41-20				924.78	4.0
C1	carbon black-1				88.09	29.5
C2	carbon black-2				42.86	13.3

The dependences of $\ln a$ as a function $\ln(-\ln x)$ and $\int(-\ln x)da$ as the function $\ln(-\ln x)$ are plotted from Eqs (7) and (8). A very good rectilinear dependence was obtained. The fractal coefficients of chosen nanomaterials are presented in Table 2.

Surface fractal coefficients determined from AFM

Atomic force microscopy (AFM) has an important application in fractal analysis because it provides data characterizing the material surface in the scale from a few nanometres to hundreds of micrometers with great precision. In the AFM method each sample is scanned in a few different places so as to obtain the view of the whole surface topography closest to the real one. In the case of powders a few molecules are chosen and the surface fragment is scanned on each of them.

The algorithms most frequently used for calculation of fractal coefficients from the AFM are: Fourier spectrum integral method, surface–perimeter method, structural function method and variable method. To determine the surface dimension by the Fourier spectrum integral method it is necessary to obtain the picture of the surface 2DFFT generating amplitude and time of the matrix. Assuming the surface function as $f(x,y)$, the Fourier transform in two-dimensional space can be expressed as [19]:

$$F(u,v) = \int_{-\infty}^0 \int_{-\infty}^0 f(x,y) e^{-j2\pi(ux+vy)} dx dy \quad (9)$$

where x and y are the spatial variables, u and v are the spatial frequencies for x and y .

The spatial spectrum of frequencies, $F(u,v)$ is the two-dimensional system consisting of the amplitude signal and the time along each direction. If the surface topography is fractal, its spatial spectrum of frequencies shows a linear distribution in the doubly logarithmic system and the surface fractal dimension can be expressed as [19]:

$$D_f = \frac{\beta+6}{2} \quad (10)$$

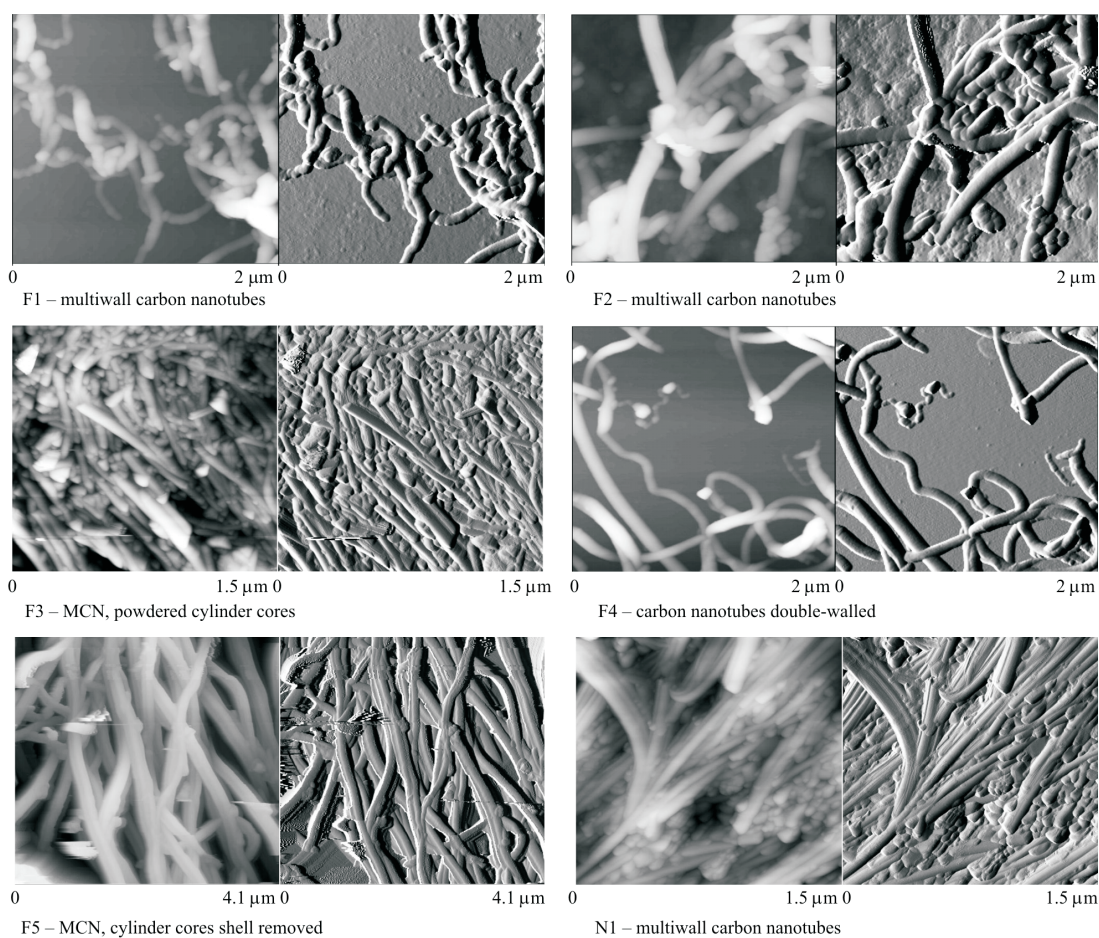
where D_f is the surface fractal dimension, β is the angle of straight line inclination.

In the Fourier spectrum integral method with the specified direction of spectrum area and the assumption that various frequencies have a common direction, a spectrum and spatial distribution of frequencies are obtained. After the double finding the logarithm, the curve of fractal dimension along a specified direction is obtained. Determining the fractal dimensions for each direction it is possible to determine the dependence between $D(\varphi)$ and the angle φ . Assuming that the angle variance in the specified range is the same angle, after averaging the spectrum amplitude the surface fractal dimension are presented in the two-polar system of the coordinates for the angles in the range $0-180^\circ$.

The surface fractal dimension characterizes irregularities of the pore surface: the larger coefficient value is reflected with more irregular and rough pore surface. The lower boundary limit of the pore coefficient 2 corresponds to the flat surface but the upper value 3 corresponds to the strongly corrugated surface, which fills up the whole space.

Table 2 Fractal coefficients of nanomaterials calculated from the sorptomatic and AFM methods

Sample	Nanomaterials	Sorptomatic method				AFM method
		Eq. (6)	Eq. (7)	Eq. (8)	average	
D1	5,6 fullerene C_{70}	2.80	2.85	2.83	2.83	2.80
B1	carbon nanotubes single walled	2.81	2.70	2.58	2.67	2.48
B2	carbon nanotubes double-walled	2.57	2.55	2.64	2.59	2.51
F1	multiwall carbon nanotube	2.68	2.62	2.57	2.62	2.47
F2	multiwall carbon nanotubes	2.57	2.61	2.47	2.55	2.46
F3	MCN, powdered cylinder cores	2.54	2.53	2.55	2.54	2.53
F4	multiwall carbon nanotube	2.64	2.57	2.59	2.60	2.45
F5	MCN, cylinder cores shell removed	2.53	2.60	2.47	2.53	2.52
F6	MCN, as-produced cylinders	2.56	2.63	2.37	2.52	2.54
N1	multiwall carbon nanotubes	2.52	2.70	2.32	2.51	2.33
N2	multiwall carbon nanotubes	2.65	2.66	2.34	2.55	2.54
N3	multiwall carbon nanotubes	2.38	2.63	2.37	2.46	2.34
M1	Na^+ [Si/Ti] MCM-41-40	2.86	2.92	2.86	2.88	2.84
M2	Na^+ [Si/Al] MCM-41-20	2.89	2.89	2.86	2.88	2.84
C1	carbon black-1	2.66	2.55	2.67	2.63	2.42
C2	carbon black-2	2.51	2.59	2.51	2.54	2.50

**Fig. 2** AFM photos of some studied nanomaterials

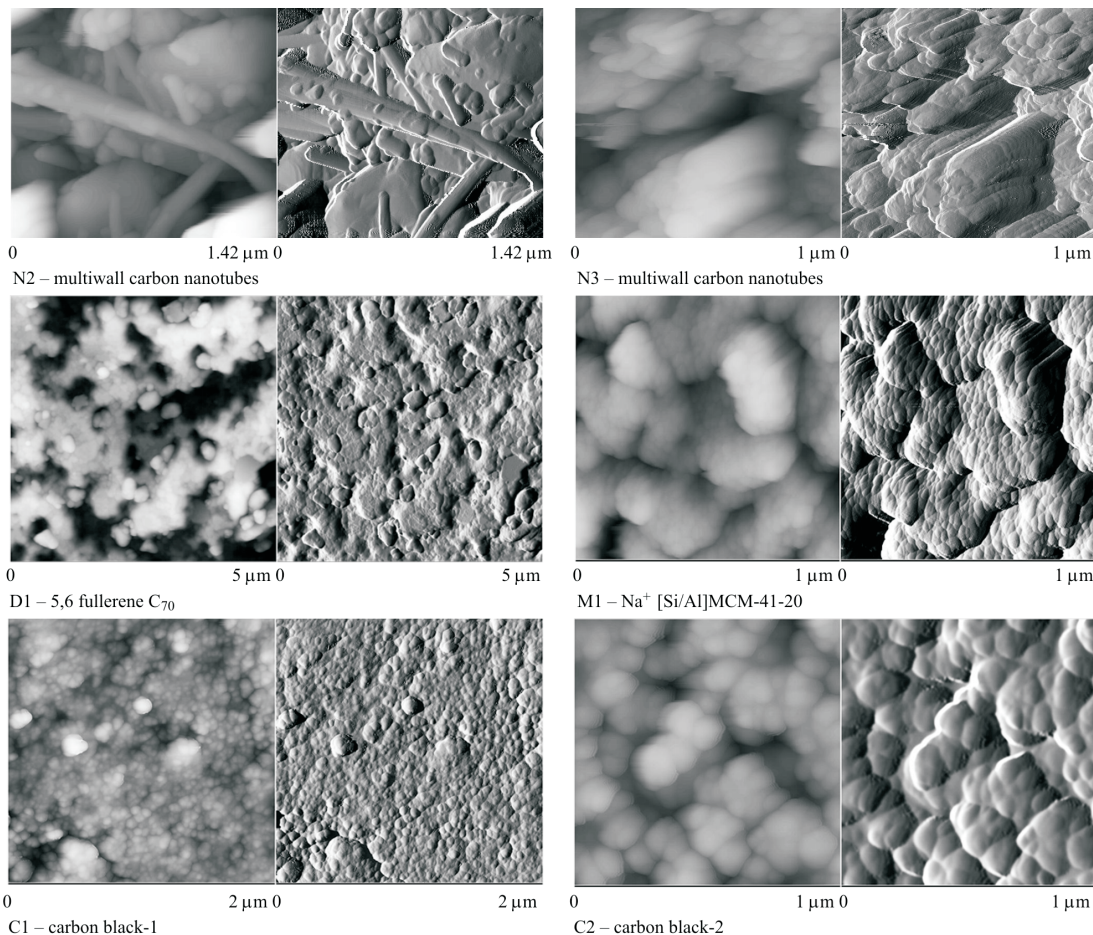


Fig. 2 Continued

Micrographs of some surfaces of studied nanomaterials made by means of atomic force microscopy are given in Fig. 2. Table 2 presents the values of pore and surface fractal coefficients of nanomaterials calculated using the data from two independent research techniques.

The highest values of fractal coefficients, over 2.80 were obtained for fullerenes and molecular sieves MCM-41. For other materials the mean values of pore fractal coefficients are in the range 2.51–2.67 but the values of surface fractal coefficients are in the range 2.33–2.58. The obtained values for pore and

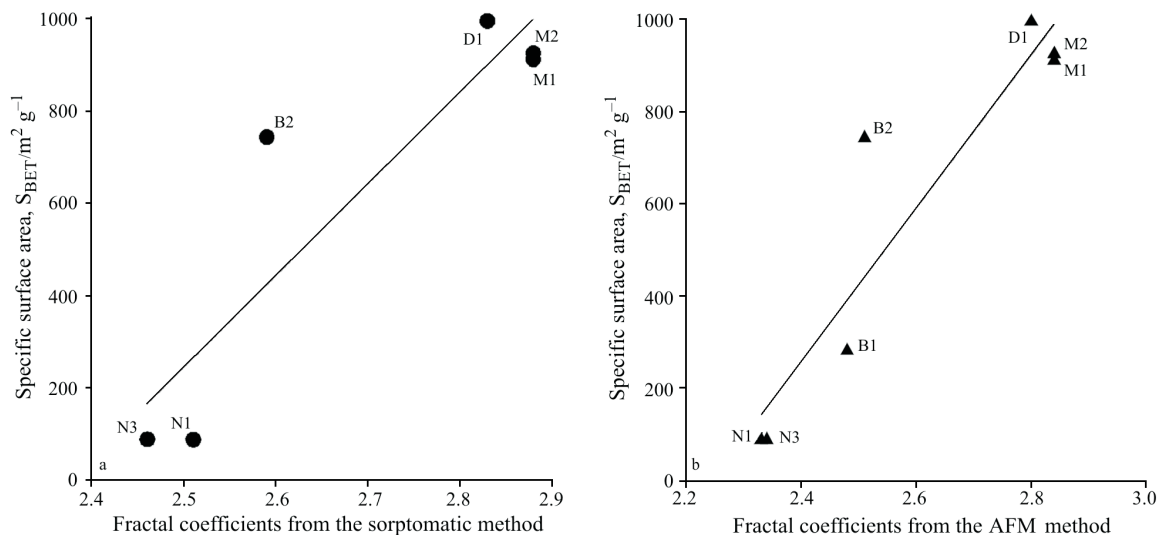


Fig. 3 The dependences of specific surface areas and fractal coefficients calculated from a – sorptomatic and b – AFM methods of some materials

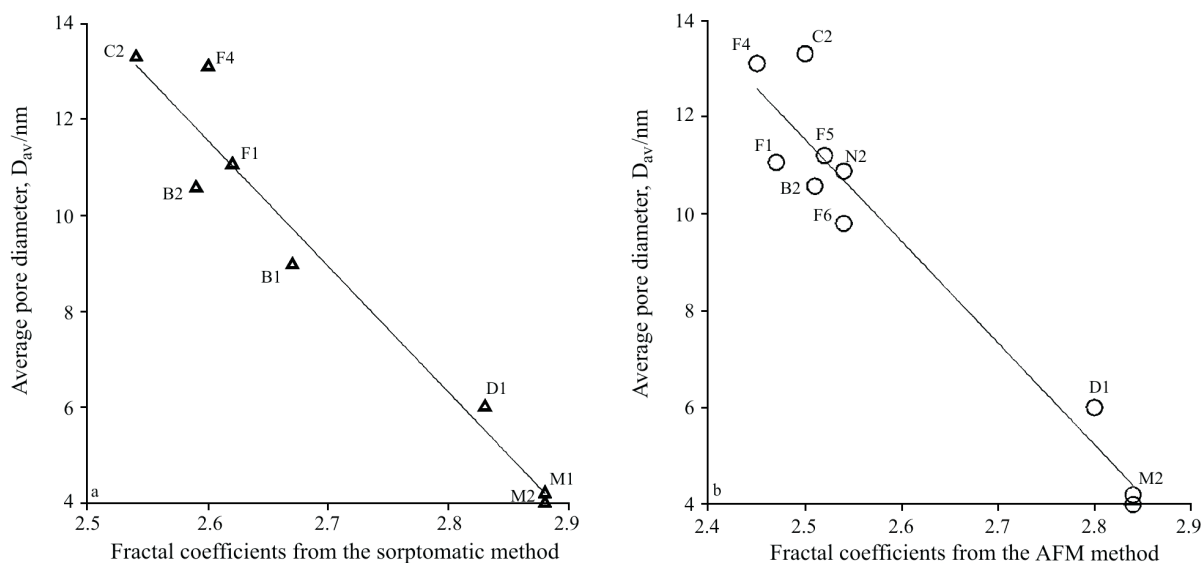


Fig. 4 The dependences of pore diameters and fractal coefficients calculated from a – sorptometric and b – AFM methods of some materials

surface fractal coefficients are comparable and indicate a relatively large extent of surface corrugation and a wide range of pore distribution in the studied nanomaterials. This is confirmed by the magnitude of specific surface area and pore distribution based on sizes of the studied nanomaterials determined from the sorptometric measurements.

Figures 3 and 4 present relationships between specific surface areas and pore diameters and fractal coefficients calculated from sorptometry and AFM methods of chosen nanomaterials. From the above figures it appears that bigger fractal coefficients have been obtained for bigger surface areas and smaller pore diameters (micropores) of surface studied.

Conclusions

Summing up, it can be stated that the methods of fractal coefficients calculation based on sorptometric and AFM measurements complement other research methods used for determination of nanomaterial porosity. Linear correlation between porosity parameters and fractal coefficients were found. Comparison of fractal coefficient values calculated from the data obtained by atomic force microscopy and those obtained by the sorptometric measurements shows good agreement.

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