

Modification of the structural parameters of coal tar pitch induced by addition of nanocarbon-coated iron at primary carbonization

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The carbon composite materials consisting of nanocarbon coated iron as additive, in different amount and coal tar pitch as matrix, was carbonized at 440 °C with the purpose to obtain materials for electromagnetic interference shielding. The materials structure and the changing induced by addition of different amount of additive were studied by Small-Angle Neutron Scattering, Electron Microscopy. The structural mode proposed exhibit two structural levels characterized by basic structural units (BSU) and fractal clusters, respectively. BSU consist of two polyaromatic molecules piled up parallel to each other. The fractal properties of the clusters depend on the amount of the additive. The effect of additive is negligible to the first level and is strongly manifested at the second level, where the small differences in amount increase the roughness or change the fractal properties from surface to mass fractal.

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1. Introduction

Carbon materials are known to have a wide range of structures, textures and properties and, as a consequence of their diversity, they have wide applications. "Carbon material" is the generic name for solid materials, which are mainly composed of carbon atoms; and it covers a large variety of materials from amorphous to highly ordered, close to the graphitic structure. In general, due to a wide variety of structures, synthetic graphite and carbon materials were in principally classified according to the possibility to develop graphitic structures and according to the production technology process. The graphitic structures are themselves classified in to non-graphitizing carbon and graphitizing carbon materials. According to the technologic production process, the carbon materials are classified in molded graphite and carbon, glassy carbon, pyrolytic carbon and graphite, carbon fibers, carbon composite, carbon and graphite powder and particles [1].

The graphitizing carbons tend to be soft and nonporous, with relatively high densities, and can be readily transformed into crystalline graphite by heating in the range of 2200-3000 °C. In contrast, the non-graphitizing carbons are hard, low-density materials and cannot be transformed to the crystalline graphite even at 3000 °C and above. The low density of the materials is a consequence of their microporous structure, which gives a high internal surface area.

Despite many industrial products and applications, and long term of research, the detailed structure of carbon materials at the atomic level is still poorly understood. One of the closest and most famous microstructural models of carbon material, which is now considered the classical one, was proposed by R. Franklin in 1951 [2].

The Franklin model (Fig. 1) assumed that the microstructure of carbon material consisted either of short fragments of graphite cross-linked by bridging groups or of a twisted network of carbon polyaromatic planar layers.

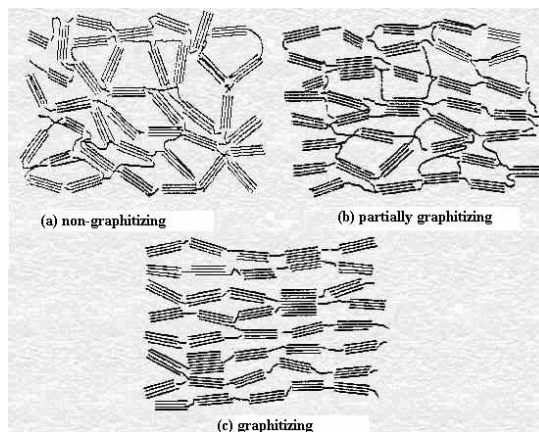


Fig. 1. Franklin model of (a) non-graphitizing, (b) partially graphitizing and (c) graphitizing carbon materials [2], where the straight lines represent the grapheme(planar polyaromatic molecules) layers and the stacks of these graphite fragments.

The structures of carbon materials are very complex and present characteristic structural features at different length scales; these are changing during the carbonization and graphitization process. The most famous model of changing induced in structure of carbon materials by heat treatment was given by A. Oberlin and presented in Fig. 2 [3]. All the carbonaceous materials contain the same elemental bricks or basic structural units (BSU). These exhibit diverse three-dimensional arrangements at different scales, according to the occurrence of the various microscopic bodies. The latter depend on the chemical composition and the amount of carbonization or graphitization process. An external modification of the chemical compositions may even deeply modify the three-dimensional arrangements of BSU [3,4].

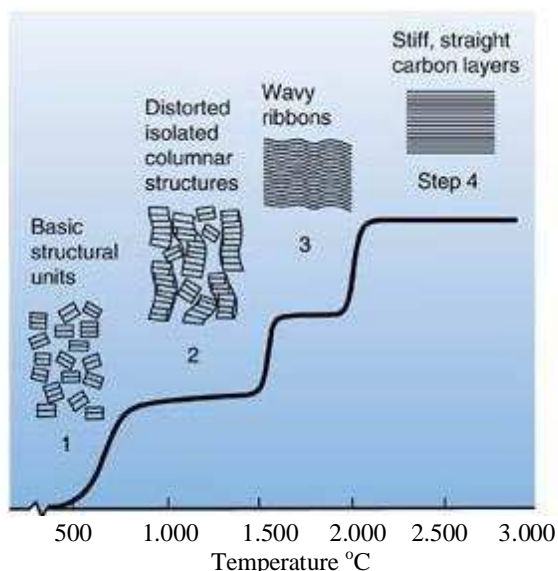


Fig. 2. The various steps of the carbonization, graphitization process [3].

The BSU consist of 2 to 4 planar polyaromatic molecules piling up parallel to each other. The number of layers in a stack, its size and arrangement in space are function primarily of the chemical properties of the starting materials and the carbonization process (rate of heat treatment, final temperature, pressure). In the early state of carbonization between the BSU here are the unstacked polyaromatic planar molecules and light hydrocarbons, they form a matrix (suspensive medium) for the BSUs. During the carbonization process the matrix (suspensive medium) are condensed and polymerized and in the end of primary carbonization are totally transformed in BSU. The arrangements of BSU are changing during the primary carbonization process from nematic order to the columnar order (mesophase spheres, which obey Brook

and Taylor model) and in the end to release to the nematic order (bulk mesophases) [5,6].

This paper presents the preparation and the structure model of some new carbon composite materials for electromagnetic shielding applications. They were obtained by dispersion of the conductive additive nanocarbon coated iron (Fe-NC) in different quantity, in a coal tar pitch (CTP), before a carbonization process, and they are been carbonized at different temperatures between 440 and 900 °C. This paper is focused on the first step, carbonization at 440 °C.

The coal tar pitch is a residuum from a coking-battery of coal and it is in generally used as a starting material or as a binder for carbon material production. The main components of CTP are mainly polyaromatic molecules with high degree of aromaticity, with aromatic hydrogen about 90%. This is one of the cheapest starting materials with wide spread industrial usage for carbonic materials and for this reason was chosen as a starting materials for our study [7].

Since Blade and Schmidt in 1985 [8] first demonstrated theoretically that the surface fractal dimension of some coal can be obtained using SAXS measurements, have been many studies on carbon materials by SAS-technique (SANS and SAXS) have been interpreted in terms of fractals structure [9-11]. The scattering curve for carbon materials presents a power-law scattering behavior with power law exponent less than 4, the deviation from the Porod law is considered to be due to the fractal properties of the materials. If the power law exponent is comprised between 2 and, the materials present mass fractal properties, specifics in carbon blacks [11]. For the power-law exponent between 3 and 4, the materials present surface fractal properties, specifics for graphitizing materials and coal [11]. For the slope equal 4 the experimental curve obeys the Porod law and the interface between the phases is smooth. The fractal dimension D_s (surface fractal dimension) and D_m (mass fractal dimension) characterizes the topology of the surface fractals and the morphology of mass fractals and is calculated from the power law exponent: if $2 < s < 3$ $D_m = s$ and if $3 < s < 4$ $D_s = 6 - s$.

In the present paper, the structure of the CTP is investigated from the point of view of the structural change induced by the addition of different quantities of additive during the primary carbonization process. The structure will be modeled according to the occurrence of the characteristic structural feature (three-dimensional bodies) at different length scale.

The goal of this research is to develop, to model and to control the structure properties of materials with respect to relationship between microstructure, physical properties, and processing condition. The aim of this study is to improve our knowledge about the material structure and the electromagnetic shielding mechanism. For this

reason, the influence of Fe-NC on the structure has been investigated by SANS (Small-angle neutron scattering).

2. Experimental method and materials preparation

2.1. Sample preparation

The CTP was processed for Quinoline insoluble (QI) removal using a modified Soxhlet. The latter was mixed with Fe-Nc powder in amount of: 1.5; 1; 0.5 weight percent. These mixtures were heat-treated at 440 °C, in inert atmosphere and with 10 °C/min heating rate. More details of the sample preparation were presented in reference [12]. The materials obtained in this way are brittle solids.

2.2. Experimental method

Electron micrography studies were carried out in the JSM-842 Scanning Electron Microscope, with the resolution 7 nm. The presented microraphies have 300,15 000, 30 000 and 70 000 magnification.

The SANS-measurements were carried out using the YuMO-Small Angle Neutron Spectrometer (JINR-Dubna), with the following characteristics: flux on the sample (thermal neutrons 1.4×10^7 n/(s*cm²), wavelength 0.5 - 5 Å (without cold moderator), wave-vector (q) range 7×10^{-3} - 0.5 Å⁻¹, background level 0.03 - 0.2 cm⁻¹ [13]. The sample for SANS measurement was ground and sieving to obtain of grains with size less than 100 microns, then the powder was put in special quartz cell with light path thickness 1 millimeters. The scattering from empty cell was measured and the scattering curve was subtracted from scattering of the samples. Smoothing procedure to SANS curves was not employed.

3. Results and discussion

The measured scattering curves for all the samples show a complex shape. All the scattering curves present flat background in the log-log representation after the extraction of the instrumental background (Fig. 3). This flat background is due to the incoherent scattering of some small quantity of hydrogen or absorbed water (hygroscopic humidity) [10]. To determine and subtract this flat background we made a first fit with equation 1 [8]. The results are listed in the Table 1.

$$I(q) = I_0 * q^{-S} + C \quad (1)$$

Table 1. The characteristic parameters of non-linear fitting of the experimental curves by equation 1, where I_0 is the scattering intensity at zero angle, S is the slope of the experimental scattering curves, C is the background, χ^2 is the fit errors.

Sample (Fe-NC.%)	χ^2	I_0 [a.u.]	S	C [a.u.]
1.5%	1.441	$6E-4 \pm 6E-5$	2.18 ± 0.03	0.29 ± 0.002
1%	1.047	$7E-6 \pm 9.6E-7$	3.31 ± 0.03	0.26 ± 0.001
0.5%	1.156	$3E-6 \pm 8.8E-7$	3.42 ± 0.06	3.42 ± 0.06
0%	2.357	$1E-6 \pm 1.7E-7$	3.78 ± 0.03	0.27 ± 0.001

The parameter C obtained in this way was subtracted from the each scattering curve (Fig. 4). Then in the log-log representation (Fig. 3) can easily observe two domains due to the different contributions. The lower q domain comprised between 0.01 - 0.05 Å⁻¹ (corresponded to the large objects, further we will named these clusters) exhibit the power law scattering behavior. We made a new linear fit in log-log coordinates on this range of q domain and the results are show in the Table 2, and indicated the presence of big clusters with fractal properties. The size of clusters ($d=2\pi/q$) are bigger than 125 Å (the upper limits cannot be determined, because are beyond the instrumental limits of the detector). The slope increases with increase the amount of the additive. All the samples present surface fractal properties with one exception for the 1.5% Fe-NC. For the latter the clusters present mass fractal properties ($D_m = s = 2.1 \pm 0.03$). The roughness of the surface fractal clusters and surface fractal dimension increase with decreasing the quantity of additive. From these we conclude that the quantity of additive have an important role in the development of the structure at this length scale. Smaller quantities (0.5-0.1) increase the roughness ($D_{S1\%Fe-Nc} = 2.87 \pm 0.04$; $D_{S0.5\%Fe-Nc} = 2.58 \pm 0.06$), induced a condensation in the skeleton of the clusters, since the bigger quantity present anti-agglutinant effect, that determines the formation of mass fractal clusters. This is confirmed and by electron micrography presented in the Fig. 5.

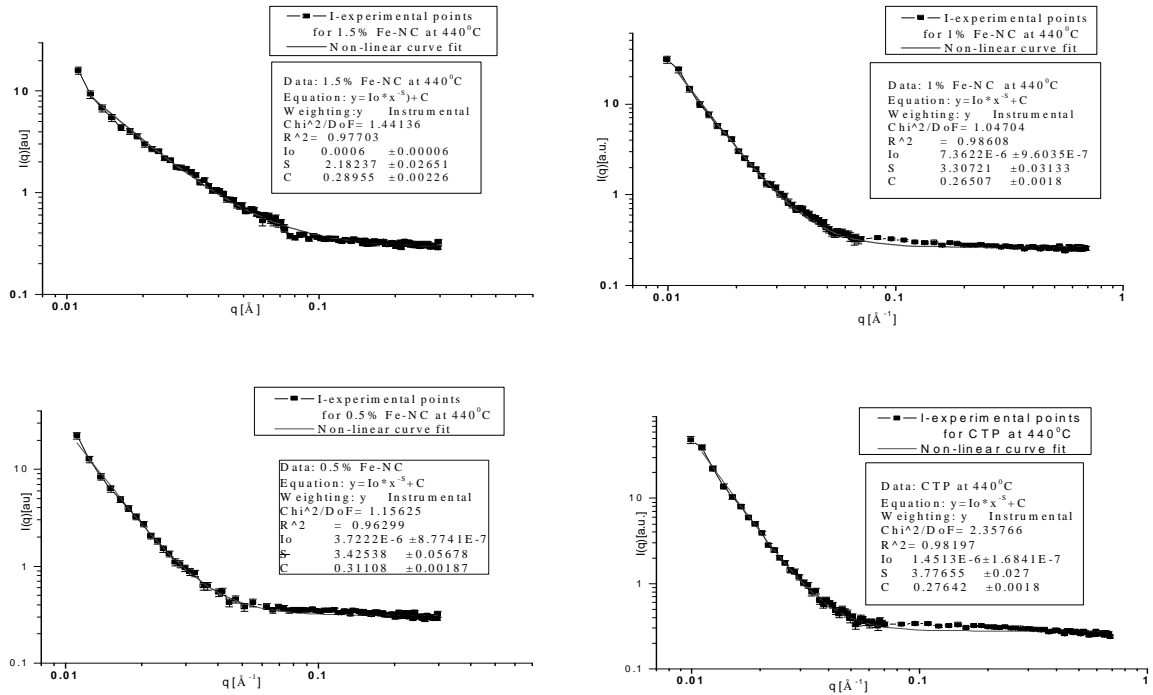


Fig. 3. Plot in the logarithmic coordinates for all the samples, fitted with non-linear curve given by equation 1.

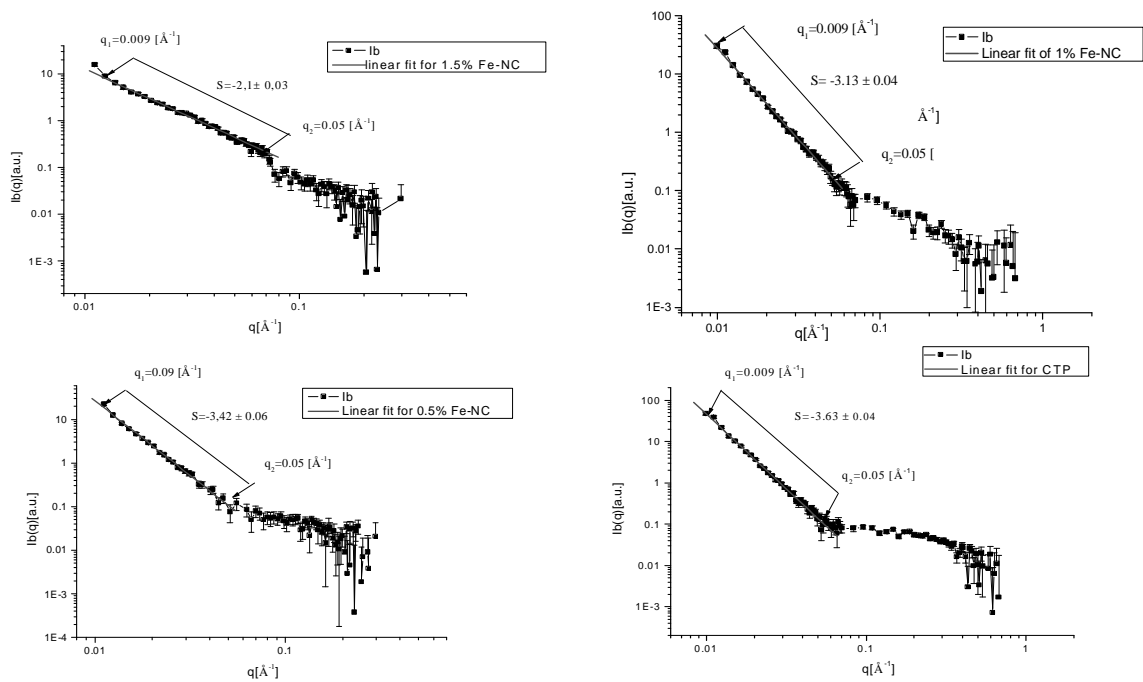


Fig. 4. Plot in the logarithmic coordinates for all the samples, after the extraction of flat background.

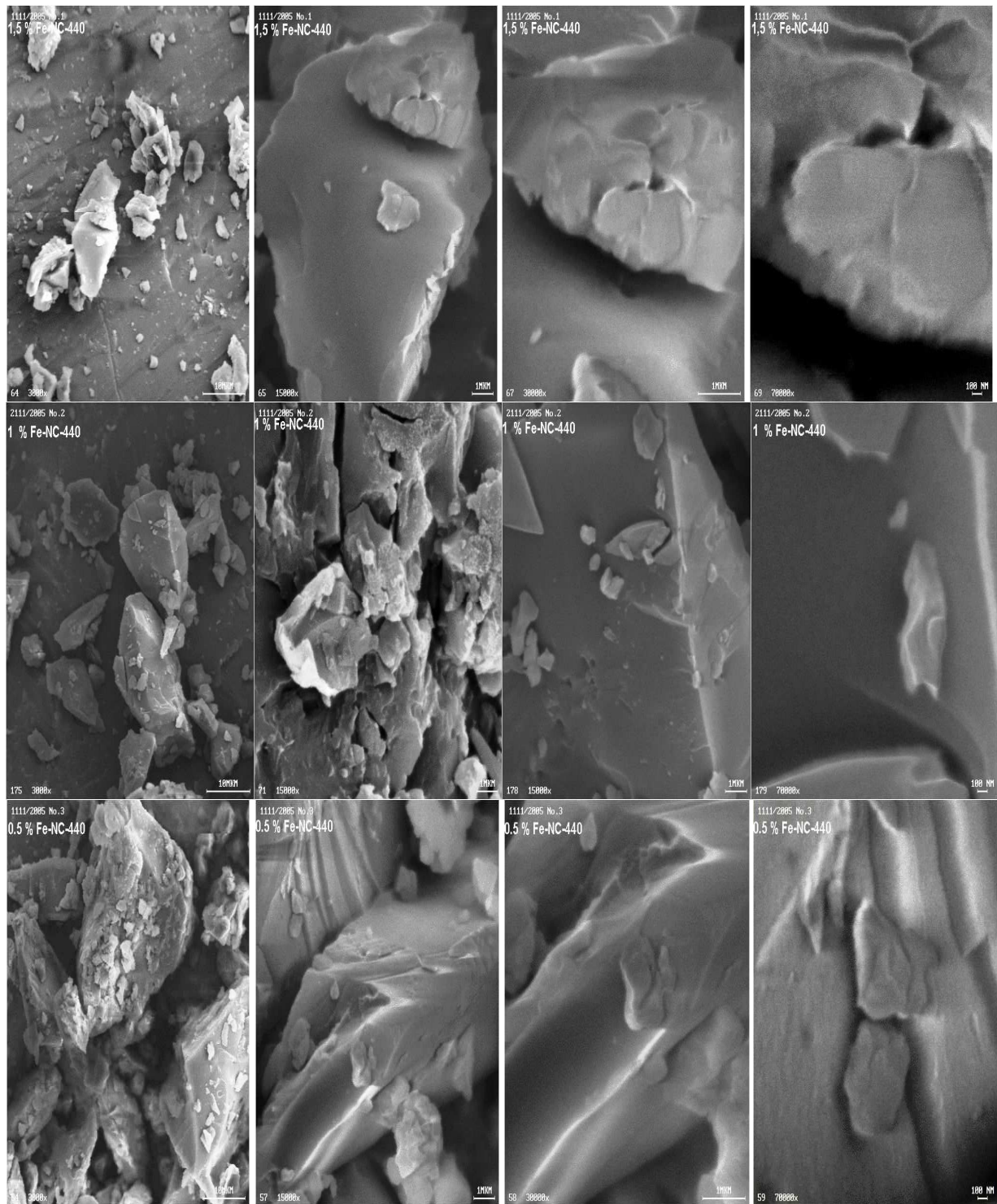


Fig. 5. Electron micrography of the Coal Tar Pitch added with different quantities of Fe-NC at 300, 15 000, 30 000 and 70 000 magnification (from the left to right).

Table 2. The characteristic parameters of linear fitting of the experimental curves, where I_0 is the scattering intensity at zero angle, S is the slope of the experimental scattering curves, D_s is the surface fractal dimension.

Sample (Fe-NC. %)	S	D_s	q_{\max} [\AA^{-1}]
1.5%	2.1 ± 0.03	$2.1 \pm 0.002^*$	0.05
1%	3.13 ± 0.04	2.87 ± 0.04	0.05
0.5%	3.42 ± 0.06	2.58 ± 0.06	0.05
0%	3.63 ± 0.04	2.37 ± 0.04	0.05

The second linear segment (large q domain) comprised between 0.07-0.7 \AA , corresponds to the inner structure of the clusters and exhibit large instrumental uncertainties. We fitted this with Gaussian model [15,16] (equation 3-4 and present in Fig. 6) and the result shown in the Table 3.

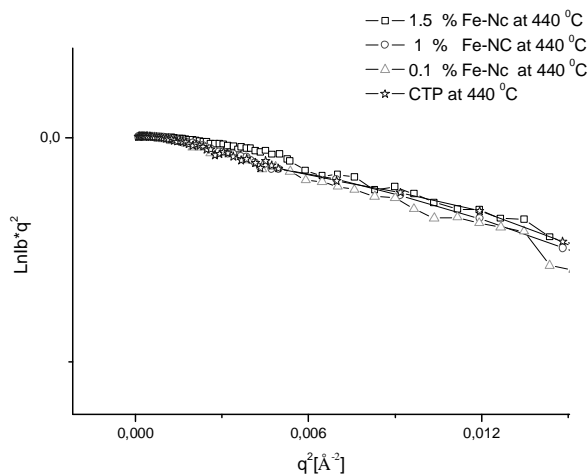


Fig. 6. Plot of Gaussian model for all the samples.

$$I_t(q) = I_t(0) \exp(-q^2 R_t^2) \quad (2)$$

$$R_{t2} = T^2 / 12 \quad (3)$$

The results are reliable if they satisfy the condition: $\frac{2\pi}{\sqrt{S_l}} \leq q \leq \frac{l}{R_t}$;

The values of thickness are close to interspacing value (d_{002}) from the graphene layer obtained usually by X-ray measurements in any graphitizing carbon materials. We consider that this confirms the existence of BSU, the smallest characteristic element for the carbon materials. The thickness value of BSU probed that BSU consists of two polyaromatic molecules piled up one on another. From the point of view of additive influence we can conclude that at this level of structure, the influence of the additive is negligible.

Table 3. BSU thickness dependence on the type of additive. The radius of gyration of the thickness R_t , and the thickness of the lamella T . The q range where the Gaussian approximation shows a straight line.

Sample (Fe-NC). %)	R_t [\AA]	T [\AA]
1.5%	1.38	3.66
1%	1.43	3.89
0.5%	1.38	3.67
0%	1.43	3.85

4. Conclusions

We proposed a structural model for CTP carbonized at 440 °C and the changing induced in the structure by addition of different quantities of Fe-Nc. The model is the result of SANS-measurements.

The model exhibits two structural levels characterized by specific structural features. First level presents as structural feature (element) the BSU. This consists of two polyaromatic molecules piled up parallel to each other. The BSUs are randomly situated, and form the inner part of the next level. The second level concerns as structural feature the clusters with fractal properties. The fractal properties depend on the amount of the additive.

The effect of additive is negligible to the first level and is strongly manifested at the second level, where the small differences in the additive amount increase the roughness or change the fractal properties from surface to mass fractal.

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