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Structural modifications induced on the Coal Tar Pitch by addition of nanotubes and nanofibers

I. ION*, C. M. MITU[a], A. BARA, YU. KOVALEV[b,c]
Carbon Materials Laboratory, National Institute for Research and Development in Electrical Engineering, 030138 Bucharest-3, Romania
[a]*Institute for Space Sciences, Bucharest, Bucharest-Magurele P.O.Box MG-23,Romania*
[b]*Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University, Moscow, Russia*
[c]*Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Russia*

The analysis of Small Angle Neutron Scattering (SANS) data from coal tar pitch carbonized at 460^{0}C with addition of 1.5 wt. % single and multiwalled nanotubes (SWNT and MWNT) is reported. A structural model consisting of two structural levels was proposed as result of SANS-data. As a structural feature, the first level presents the clusters with surface fractal properties and diameter not less then 1000 Å. The second level consists of the basic structural units (BSU), which form the inner part of the first level. The type or/and size of the additives have a key role in the development of the structure at this length scale.

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1. Introduction

In the past, the industry of coal tar pitch (CTP) was closely associated with that of metallurgical coke and aluminium industry. Now, approximately 75% of the total consumption of CTP is used as binder in the production of carbon anodes for aluminium industry, 12% as binder for graphite electrodes for electrical arc furnace and impregnating pitch for densification. The last 23% for production of metallurgical coke, fibres, binder and impregnating pitch for different kinds of composite materials [1, 2].

Now the greatest interest is in understanding the mechanism of pitch carbonization, and the optimization of the industrial production. Many factors can biass the transformation of the pitch into the carbon. Among these the most important are: experimental conditions (final temperature, soaking time, heating rate, pressure, and experimental device), composition of pitch and role of its own particles or added solid particles [1, 2]. In order to improve and optimize the mechanical, electrical and chemical properties of carbon materials (CMs) the addition of solid particles has been widely used as a procedure to modify the pyrolysis behaviour of pitches. These particles include, for example, graphite [3], carbon blacks [4,5], coke [1], fullerene [6, 7], silica [8], boron [9].

It has been pointed out that CMs present structural features at different length scales; and these are changing during the carbonization and graphitization process, and the key role is kept by the chemical composition of starting materials [10-13]. All carbonaceous materials contain the same elemental bricks named basic structural units (BSU) [10].

The present study is focused on the influence of additives on the pyrolysis behaviours of CTP and the structural modifications induced in its structure. Single and multiwalled nanotubes (SWNT and MWNT) were used as additives in the present study.

Electron microscopy (EM) micrographs from the graphitizable CMs, carbonized at low temperature, show textureless characteristics. These characteristics are visible after the extraction of the carbonaceous mesophase using different strong solvents (quinoline, tetrahidrofuran, antrachinone). The extraction content is strongly influenced by the type of solvent and time reaction. Electron microscopy (EM)-techniques covers the same range as SANS-techniques from 1 to 1000 Å. In opposite, SANS-technique is non-destructive technique, does not influence the characteristic features of samples and proves the average characteristic of materials. For this reason it is necessary to use SANS techniques, which is more suitable than EM, to investigate the structural features of materials in this range. Our purpose in this preliminary work is to introduce the SANS technique for CMs characterization. Other advantages of using SANS are: a non-destructive technique; does not influence the characteristics of samples and provide an average description of materials characteristics.

Bale and Schmidt [14], first demonstrated theoretically that the surface fractal dimension of some coal can be obtained using SAXS measurements. There are many studies on CMs structure by SAS-technique (SANS and SAXS) which have been interpreted in terms of fractals structure [14-18]. The CMs present a power-law scattering behaviour with a value of the power-law exponent P 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 P is comprised

between 1 and 3, the materials present mass fractal properties, characteristic for carbon blacks [18]. For the power-law exponent P between 3 and 4, the materials present surface fractal properties (SFP), characteristic for graphitizing materials and coal [18]. For the power-law exponent P equal to 4, the experimental curve obeys the Porod law and the interface between the phases is smooth and sharp. The fractal dimensions characterize the topology of the surface fractals and respectively the morphology of mass fractals, and were calculated from the power-law exponent P as:

surface fractal dimension D_S= 6-P, if 3< P<4 and mass fractal dimension D_M=P, if 1< P< 3.

Becaucage [19] developed a general equation capable to describe scattering functions containing multiple length-scales. With this it is possible to analyze SAS data obtained from systems that consist of multiple structural levels. One structural level is described by a Guinier regime (the first term of Eq. 1.) and an associate power-law regime (the second term of Ec. 1) [19].

$$I(q) = G_{exp}\left(-\frac{q^2R^2}{3}\right) + B\left\{\frac{[erf(qkR/2.45)]^3}{q}\right\}^P \quad (1)$$

We denoted by G the Guinier prefactor, R the gyration radius, B the power-law coefficient, P the power-law exponent, k is a coefficient which describes the degree of correlation.

For two-level structures the unified exponential/power-law approach is given by the relation 2 [19].

$$I(q) = G_1\exp\left(-\frac{q^2R_1^2}{3}\right) + B_1\exp\left(-\frac{q^2R_2^2}{3}\right)\left\{\frac{[erf(qkR_1/2.45)]^3}{q}\right\}^{P_1} + G_2\exp\left(-\frac{q^2R_2^2}{3}\right) + B_2\left\{\frac{[erf(qkR_2/2.45)]^3}{q}\right\}^{P_2} + C \quad (2)$$

Where: G_1, G_2, B_1, B_2, P_1, P_2, R_1, R_2 – are the parameters which describe the first and, respectively, the second structural level.

The unified exponential/power-law approach can distinguish Guinier regime buried between two power-law regimes. This approach is applicable to wide variety of systems [19, 20].

2. Experimental method and material preparation

Primary Quinoline insoluble fraction was removed from CTP by a reflux–Soxhlet extraction method. The soluble fraction in quinoline was mixed with 1.5 wt. % SWNT and MWNT and heated at 460^{0}C, with 10^{0}C/minute heating rate, in an inert atmosphere and one-hour soaking time. The CMs powder with grains sizes less than 100 μm was put in Hellma quartz cell with light path thickness 1 mm and thermostat-box Lauda (20^{0}C±0.3^{0}C). The SANS-measurements were performed using the YuMO spectrometer (JINR, Dubna) [21]. A standard calibration procedure was used, background and container correction was performed. Smoothing procedure was not employed to SANS curves [21].

3. Results

SANS data present complex shapes in log-log representation (Fig. 1). Two regimes of scattering intensity at different length scales are easily observed due to two the different contributions.

We made a linear fit for the upper linear part of curves in log-log coordinates. The results are presented in Table 1.

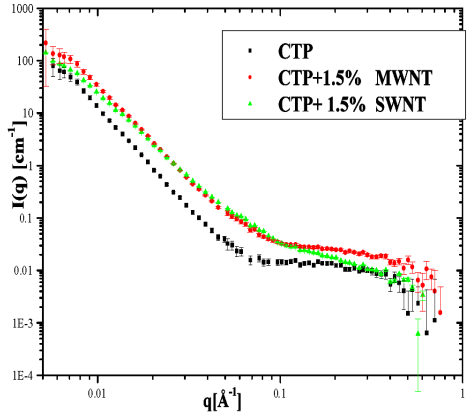

Fig 1. SANS curves of CTP with different additives.

Table 1. The characteristic parameters of linear fitting for the upper linear part of the experimental curves.

Sample	D_{S1}	R_{max} [Å]	R_{min} [Å]
CTP	2.18 ± 0.03	795 ± 31	72 ± 1
SWNT	2.74 ± 0.02	785 ± 43	32 ± 1
MWN	2.37 ± 0.02	815 ± 52	35 ± 1

The results indicate the presence of carbonic clusters with SFP characterized by surface fractal dimension D_{S1} and clusters radius R. The size of clusters are not smaller than R_{min} (R_{min}~π/q_{max}). More precise value cannot be determined because the upper limits are beyond the instrumental limits of the setup.

The SANS data was fitted with Eq. 2 (Fig. 2). We excluded the first term because the experimental curves do not present Guinier regime for big particles. The results are presented in Table 2. The result from linear fit, the fit with unified exponential/power-law approach, and the

values from complementary analysis are in good agreement (Table 2.).

The first level consist of carbonic clusters with surface fractal properties characterized by surface fractal dimension D_s= 6-P_1 and radius of gyration R_1.

The second level consists of elemental units characterized by radius of gyration R_2, and power law coefficient P_2. The results are well fitted with the description of the BSU from literature [10]. The tail of the curves and the fit results in this region are strongly influenced by the presents of hydrogen, and residual metals, which are present in ppm. amount in the CMs, increasing the multiscattering effects, respectively the experimental errors.

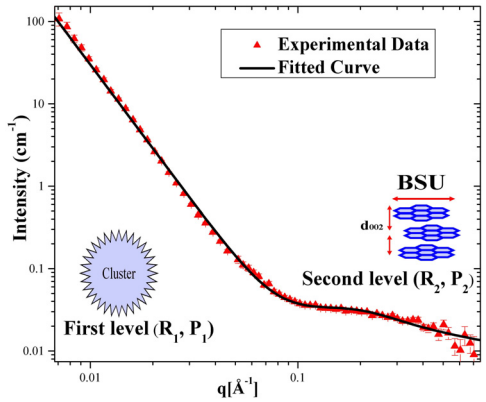

Fig. 2. The neutron scattering curve for CTP with 1.5% MWNT, fitted with Eq. 2.

Table 2. The characteristic parameters of SANS curves fitted with eq.2, where P_1-power-law exponent for level 1, P_2-power-law exponent for level 2, R_1-radius of gyration for level 1, R_2- radius of gyration for level 2, and C-background.

Sample	χ^2	R_1[Å]	P_1	R_2 [Å]	P_2	C [$g^{-1}cm^2$]
CTP	0.99	487±49	3.92 ± 0.04	15 ± 0.3	1.23±0.31	0.1 ± 0.002
SWNT	1.28	396±22	3.3 ± 0.03	14 ± 2	2.57±0.6	0.11 ± 0.011
MWNT	1.09	453±30	3.58 ± 0.02	15 ± 1	1.11±0.31	0.09 ± 0.015

4. Conclusions

We proposed a structural model, resulted from SANS-measurements of CTP carbonized at 460^0 C with addition of 1.5 wt. % SWNT and MWNT. It consists of two structural levels characterized by distinct features. The first level consists of clusters with SFP and diameter not less than 1000 Å. The BSU is the structural feature of the second level and the BSU units form, by aggregation, the inner part of the next level.

The surface properties of carbonic clusters are changing with addition process. The additive increases the surface roughness, and the SWNT proved an emphasized effect in this way.

In conclusion the type or/and size of the additives have a key role in the development of the structure at this length scale. The effect of additives is negligible for the second level and is strongly manifested at the first level, where a small difference in type or/and size of the additives induce important differences in the roughness of the clusters surface.

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*Corresponding author: ionioanamitu@yahoo.com

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