Carbon materials on the base of inorganic-organic polymer nanocomposite precursors

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Carbon materials with very good mechanical properties and SiC are produced from inorganic-organic polymer nanocomposite precursors. It was found that the main factor which determines the excellent mechanical properties of the obtained material is the interaction of the binder (PAN) with the filler (silica and zeolite). The "baking criterion" was used for estimation of the interaction between filler and binder during formation and heat treatment of the initial composites. The corellation between the „baking criterion" and the compressive strength of the obtained material was determined. Pressing of the compositions is of big significance for improving the surface contact between the binder and the filler.

Key words: inorganic-organic polymer, silicon carbide, carbon, silica.

1. INTRODUCTION

The combination of the characteristics of synthetic polymers (elasticity, reduced density and easy processability) with those of inorganic materials (hardness, thermal stability and large availability) opens new perspectives for obtaining new materials on the base of inorganic-organic composites. The synthesis and the applications of inorganic-organic nanohybrids were developed mainly in the last decade [1-7]. There are four important methods for obtaining of hybrids based on organic polymers and inorganic oxides [8]:

- The polymer and the inorganic component are formed simultaneously by a process, for example, sol - gel polymerization process [9-10];
- The polymer is formed by direct polymerization on the surface or in the pores of the already synthesized oxide material [11-12];
- The inorganic oxide compound is formed in a polymer by a sol - gel process (for example, biomineralization) [13-14];
- Both components are previously prepared and react one with another and/or form a hybrid network through interpenetrating reactions [15].

The properties of the obtained materials depend on such factors as shape and size of the filler particles, composition of binder and interaction between the components [16].

During the preparation of the composition, part of the binder molecules are adsorbed on the surface of the filler particles. These molecules could interact with the filler surface and with other substances in the adsorbed part of the binder. It was found that in order to characterize this interaction, it is appropriate to use a "baking criterion" proposed for the assessment of the baking ability of the pitches [17]. The "baking criterion" permits [18] the qualitative characterization of the degree of interaction between filler and binder and is determined by the expression:

$$\Delta K = (\frac{100.K_c - M_f K_f}{M_b K_b} - 1).100$$

where ΔK = "baking criterion", %
K_c = amount of the solid residue of the composite, %
K_f = amount of the solid residue of the filler, %
K_b = amount of the solid residue of the binder, %
M_f = amount of the filler in the composite, %
M_b = amount of the binder in the composite, %

ΔK is the increase in the solid residue of the binder when it is in the composition with the filler, and takes into account the interaction between binder and filler during the preparation of the carbon material.

2 EXPERIMENTAL

Raw materials

Mesoporous silica was obtained in the INCDMNR-IMNR (National Research – Development Institute for Non-ferous and Rare Metals – Bucarest, Romania) laboratory and was used as received.

The synthetic zeolite HZSM-5 was supplied by UPG (University for Oil and Gases – Ploiesti, Romania) and was used as received.

Inorganic-organic polymer nanocomposite synthesis and analysis of the products

The inorganic powder (silica, HZSM-5) was soaked in acrylonitrile (containing 1% azo-bis-isobutyronitrile based on monomer) in 50 mL glass ampoules. The monomer was introduced in different volume/weight ratios to silica (Table 1) and to HZSM-5 (Table 2), and the ampoules were purged with nitrogen for 10 min, in order to avoid the possible inhibition effect of oxygen. Then, the ampoules were sealed with a rubber tube and were tightened with a Hoffman clamp. For silica, the samples were named P1-P6 s-PAN, respectively, and for HZSM-5 zeolite, the samples were named P1-P6 z-PAN. Inhibitions were performed in the sealed ampoules in an Elma S10 Elmasonic ultrasonication bath containing water, for 1 h. After that, the ampoules were kept for 24 h at room temperature without ultrasonication. Finally, a new 1 h ultrasonication was applied. The composite materials were obtained by the introduction of the glass ampoules in an ultra-thermostated water bath at 65°C. Although the initiator concentration becomes practically 0 after 10 h, the ampoules were kept 24 h for polymerization, in order to ascertain that the monomer conversion is practically complete, eliminating any doubt of monomer presence in the composite. In these conditions the polymerization of acrylonitrile within the silica or HZSM-5 pores occurred.

Thermogravimetry of the composites was performed on the Q600 TA Instruments analyzer, using air atmosphere from 20°C to 700°C using 10°C/min rate.

Analysis of heat- treated pellets "baking criterion" determination

The "baking criterion" was determined by preparation of pellets from s-PAN and z-PAN composites using pressing in a press form and baking the pellets at a heating rate of 1°C/min up to 800°C. The solid residue from the filler (silica or zeolite) - K_f and from the binder - K_b (PAN) was determined under the same conditions.

Pellets from composites were first heat-treated up to 1300°C and then up to 1600°C at a heating rate of 5°C/min. All investigated composites were characterized by X-ray diffraction analysis on a Bruker D8 Advance diffractometer using CuKα radiation, and by scanning electron microscopy on a Philips 515 instrument. The average crystallite size was calculated according to the Scherrer formula by using the Topas V3 programme [19].

3. RESULTS AND DISCUSSION

Compositions of silica/PAN and zeolite/PAN were prepared in the proportions presented in Tables 1 and 2.

Table 1. Composition of silica and acrylonitrile samples, precursors for obtaining nanocomposites

Sample	Silica (g)	Acrylonitrile	
		(mL)	(g)
P1 silica-polyacrylonitrile	2.0	1.5	1.20
P2 silica-polyacrylonitrile	2.0	1.8	1.44
P3 silica-polyacrylonitrile	2.0	2.0	1.60
P4 silica-polyacrylonitrile	2.0	2.2	1.76
P5 silica-polyacrylonitrile	2.0	2.5	2.00
P6 silica-polyacrylonitrile	2.0	2.8	2.24

Table 2. Composition of zeolite and acrylonitrile samples, precursors for obtaining nanocomposites

Sample	Zeolite HZSM-5 (g)	Acrylonitrile	
		(mL)	(g)
P1 zeolite-polyacrylonitrile	2.0	4.5	3.60
P2 zeolite-polyacrylonitrile	2.0	4.8	3.84
P3 zeolite-polyacrylonitrile	2.0	5.0	4.00
P4 zeolite-polyacrylonitrile	2.0	5.2	4.16
P5 zeolite-polyacrylonitrile	2.0	5.5	4.40
P6 zeolite-polyacrylonitrile	2.0	5.8	4.64

DTG (diffential thermo-gravimetric) analysis of silica/PAN and zeolite/PAN composites is presented on Fig. 1. The curves indicate two main intervals of weight loss, 280-360°C and 440-640°C, for both composites. The first interval is due to the beginning of polymer degradation. The second interval corresponds to processes of deep degradation, which finish with cyclization of the
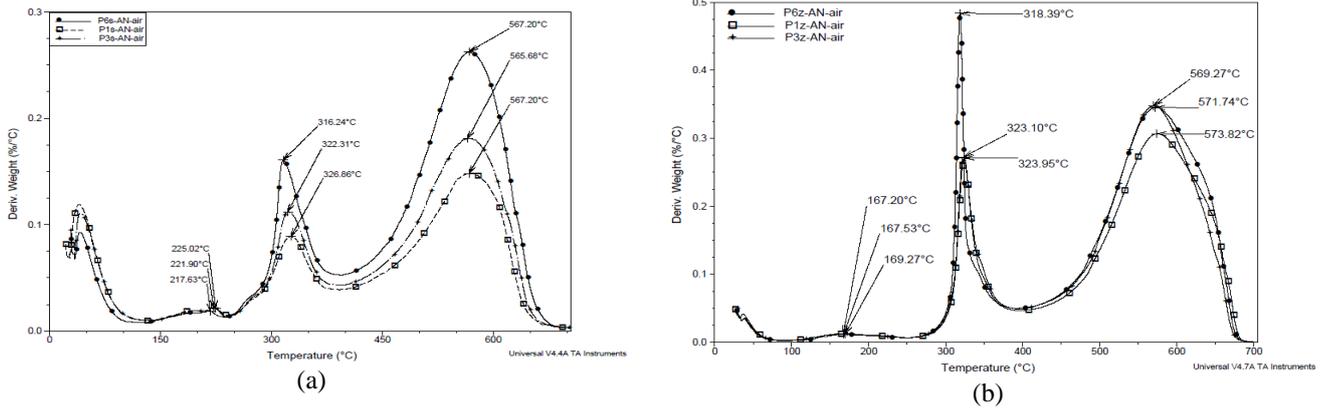
Fig. 1. DTG curves for silica/PAN (a) and zeolite/PAN (b) composites.

polymer and formation of the final structure of the material for this stage.

Fig. 1 shows that the temperatures of the beginning of the main intervals of weight loss increase with increasing the content of the filler (silica and zeolite) in the composite. At the same time the weight loss decreases with increasing the content of filler in the composite. This is due to the extended interaction between filler and binder in the composite ias a result of the increased filler content. The results reveal a considerable influence of the interaction between the filler and the binder in the composite on the processes occurring during heat treatment of the composite.On the base of the results of the DTG analysis, the temperature of heat treatment of pellets of composites for determination of the "baking criterion" was determined as 800°C, *i.e.*, when the reaction of degradation is completed and the synthesis passes through carbonization of the polymer part of the composite.

„Baking criterion"

Investigations were carried out to assess the baking ability of PAN in composition with silica and zeolite. In Tables 3 and 4 data are presented for the "baking criterion" and the compressive strength of the composites containing different amounts of binder.

The yield of solid product from PAN after heating up to 900°C is 42.1% in argon atmosphere.

The yield of solid product from silica after heating up to 900°C is 91.1%; from the zeolite it is 81.1%, in argon atmosphere for both.

The yield of solid product from polymer in the pellets was calculated using equation:

$$\Delta Y_p = (\frac{Y_p - Y_s}{Y_p} - 1) \times 100 = (\frac{Y_p - aY_s}{bY_p} - 1) \times 100$$

where: Y_p – solid yield from pellets;

- Y_s – solid yield from pure silica at the same temperature - 900°C;
- Y_p – solid yield from pure polymer at 900°C;
- a – amount of silica or zeolite, respectively, in the composite;
- b – amount of polymer in the composite.

Table 3. Data for the heat treatment up to 800°C of pellets of silica/PAN composites

Sample	Solid yield %	Increase of solid yield from polymer in pellets, %	Compressive strength, MPa
P_{1S}	69.5	19.9	4.0
P_{2S}	68.9	23.9	5.0
P_{3S}	68.2	24.5	8.0
P_{4S}	67.2	22.3	7.0
P_{5S}	65.9	20.9	6.0
P_{6S}	63.8	15.3	6.0

Table 4. Data for the heat treatment up to 800°C of pellets of zeolite/PAN composites

Sample	Solid yield, %	Increase of solid yield from polymer in pellets, %	Compressive strength, MPa
P_{1Z}	62.2	10.4	6.0
P_{2Z}	61.9	11.4	7.0
P_{3Z}	60.3	7.1	6.0
P_{4Z}	58.8	3.2	5.0
P_{5Z}	58.7	5.2	5.0
P_{6Z}	57.6	3.7	5.0

These data indicate that due to the interaction between polymer and silica or zeolite, respectively, the solid yield from the polymer in the composite (especially as pellets) significantly increases in comparison with the solid yield from pure polymers. It seems that the increase of the solid yield depends on the proportion of the polymer and silica or zeolite, respectively, in the composite. The data show that, with the increase in binder content in the composite, ΔK increases to a definite value. The further increase of the binder amount results in

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a decrease of ΔK. When increasing the solid yield from polymer in the composite, the compressive strength of the obtained material increases. Obviously, there is a correlation between the solid yield from the polymer in the composite and the compressive strength of the final material. The lower increase of the solid yield from PAN in the composite with zeolite, in comparison with the composite with silica, is in the result of the much higher amount of PAN in these composites. The mechanical properties of the samples obtained for silica/PAN and zeolite/PAN composites are very good. The data show that the mechanical properties of the pellets obtained from the silica/ PAN composite, are better than these of the pellets obtained from the zeolite/PAN composite.

This is due to the higher proportion of the filler in the silica/PAN composite, which leads to stronger interaction between the filler and the binder, and a subsequent increase in the mechanical strength of the obtained material. This is also confirmed by the values of the "baking criterion", which correlates with the mechanical strength characteristics of the material.

In order to increase the mechanical strength and to obtain SiC, after determination of the "baking criterion", the pellets were first heated up to 1300°C, and then up to 1600°C. As a result, the mechanical strength of the pellets was increased up to 10 MPa. In Figs. 2 and 3 the results from the XRD investigations of the pellets obtained from silica/PAN and zeolite/PAN composites heated first up to 1300°C (Fig. 2) and then up to 1600°C (Fig. 3) are presented.

Fig. 2 shows the X-ray diffraction spectra of pellets obtained from silica/PAN and zeolite/PAN composites heated up to 1300°C. In the XRD pattern (Fig. 2) of a pellet obtained from a zeolite/PAN composite, a peak at 2Θ=24° was detected. This peak corresponds to the 002 reflex of carbon and it is characteristic of the interlayer spacing in graphite. In this case the peak 002 is more narrow and asymmetric, indicative of highly ordered structure, than in the case of pellets obtained from silica/PAN composite. The main reason for this is the significantly higher filler content in silica/PAN composites in comparison with zeolite/PAN composites, because the filler particles hinder the structuring of the material and the formation of bigger crystallites during thermal treatment.

Fig. 3 shows the X-ray data for a material obtained from silica/PAN and zeolite/PAN composites and heated up to 1600°C. The data
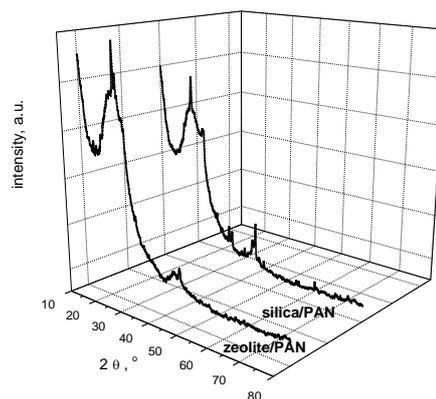
Fig. 2. X-ray diffraction patterns of pellets heated up to 1300°C.
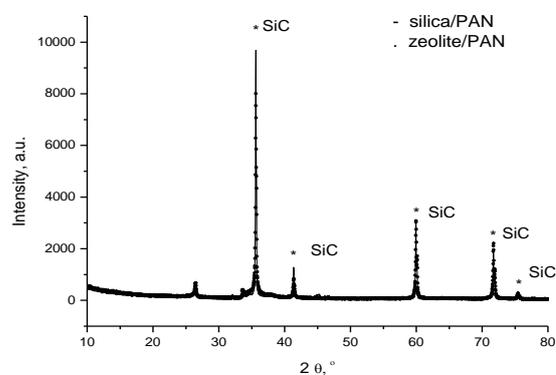
Fig. 3. XRD of the material obtained from composites silica/PAN and zeolite/PAN.

show that as a result of heat treatment, SiC is obtained from both composites (silica/PAN and zeolite/PAN).

6. CONCLUSIONS

These preliminary results point to the possibility of producing materials with high compressive strength by formation of pellets from inorganic-organic polymer nanocomposites and heating them up to 1300°C, as well as for the synthesis of SiC by heating the pellets up to 1600°C. Major factor which determines the excellent mechanical properties of the obtained materials is the interaction of the binder (PAN) with the filler (silica or zeolite) – this interaction can be estimated by means of the "baking criterion". Pressing of the compositions is of big significance for improving the surface contact between the binder and the filler.

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ВЪГЛЕРОДНИ МАТЕРИАЛИ НА ОСНОВАТА НА ОРГАНО-НЕОРГАНИЧНИ ПОЛИМЕРНИ НАНОКОМПОЗИТНИ ПРЕКУРСОРИ

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(Резюме)

Бяха получени въглеродни материали и SiC с много добри механични свойства, използвайки органо-неорганични полимерни нанокомпозитни прекурсори. Беше установено, че основният фактор, определящ отличните механични характеристики на получения материал е взаимодействието на свързващото вещество (PAN) с пълнителя (SiO₂ или зеолит). Бе използван т. нар. „критерий за спекаемост" за оценка на взаимодействието между пълнителя и свързващото вещество в процеса на формиране на композитите и термичната им обработка. Бе установена зависимост между "критерия на спекаемост" и механичната сила на якост на получения материал. Пресоването на композициите е от голямо значение за подобряване на контакта между повърхностите на свързващото вещество и на пълнителя.