

# Preparation and properties of carbon/carbon and polymer/carbon porous monolithic composites

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## Properties

### ABSTRACT

**Purpose:** An overview of own works on preparation of monolithic carbon/carbon and polymer/carbon composites, that were fabricated using natural biological precursors for both composite components: carbonized plant stem for a support and chitosan or furfuryl alcohol for a filler, is presented. Composites based on monolithic porous supports prepared from expanded graphite are also discussed.

**Design/methodology/approach:** The supports were prepared by carbonization of plants stems or by compression of expanded graphite. Next step was infiltration with the polymers, that were cross-linked on the supports. The structure and properties of the supports and the composites were characterized using numerous experimental techniques: thermogravimetry, helium gas densitometry, mercury porosimetry and adsorption of N<sub>2</sub> gas, ultrasonic and electrical measurements, FTIR, EPR and observed with microscopes: optical, SEM and TEM.

**Findings:** The carbon based composites were found to exhibit properties of the polymeric fillers, as well as electrical conductivity and high stiffness of monolithic carbon framework.

**Practical implications:** The materials could be utilized as adsorbents/absorbents, catalysts supports, sensors, filters, etc.

**Originality/value:** New class of original biodegradable bio-composites in the form of monoliths of optional shapes was obtained in contrast to adsorbents usually fabricated as granules or to composites being resins fulfilled by granules or fibres.

**Keywords:** Graphite backbone; Biotemplating; Chitosan; Polyfurfuryl alcohol (PFA); Adsorbents

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## 1. Introduction

Carbon occurs in a great number of forms. These forms differ from each other in the way the carbon atoms are bonded to each other. As a consequence, these forms of carbon differ greatly in their structure and properties e.g., diamond, graphite, fullerenes, carbon black, glassy carbon, etc. [1]. One of them - graphite -

consists of layers of carbon atoms, that can be easily exfoliated. This kind of carbon material, i.e., exfoliated (or expanded) graphite (EG) can be used as monolithic porous support for preparation various composites of a given bulk porosity [2-4]. On the other hand, because of strong polluting of our natural environment, it is necessary to find and investigate new, renewable resource materials of a natural origin. Biomass feedstocks including wood

or agricultural residues and byproducts or dedicated energy crops usually applied as biomass fuels are of significant interest, because they form the world's third largest primary energy resource. However, some of these plants, after carbonization under highly controlled conditions become the materials of various applications, especially for removal of organic and inorganic pollutants from industrial processes. Of course, carbonized dried stems are not allotropes of carbon, but owing to high content of carbon and some structure ordering, they belong to carbon materials, more precisely, to carbonaceous materials [5-8].

Generally composites containing carbon materials are built from polymer matrix, e.g., resin and crumble carbon filler. For the preparation of these composites, EG is used as a powder, while plants raw and carbonized are used generally also as powders, and as short fibres. Obtaining porous composites by coating internal surface of stiff monolithic porous skeletons from carbonized plants or compressed EG is rather rare. Figure 1 shows different structures of composites with carbonized plants used either as a filler or as a matrix (stiff skeleton).

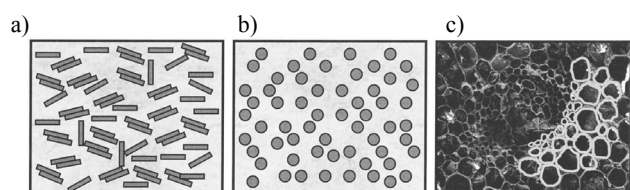


Fig. 1. Different models of two-component composites with carbonized plant: short fibres (a) and a powder (b) as a filler, flooded in a continuous polymer matrix, and (c) carbonized plant stiff skeleton (matrix), covered by thin layer of a polymer (filler)

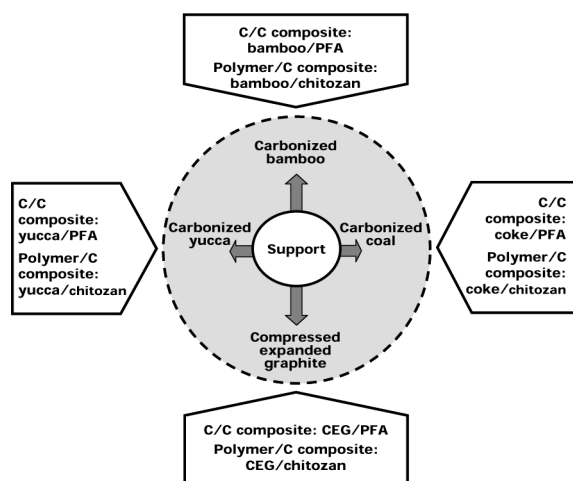


Fig. 2. Scheme showing the polymer/C and the C/C composites studied in our laboratory

Porous carbon materials such as compressed expanded graphite giving monolithic blocks after compression under various pressures and carbonized pieces of plant stems are alone useful in removal of dangerous pollutants. More interesting task is to fabricate novel composites on the basis of both compressed EG and plant carbons,

but of more rich scale expected for potential utilization of these materials. As plant carbons, two vascular plants, i.e., bamboo and yucca after highly controlled carbonization were used as supports for preparation of the composites. Two polymers of natural origin, i.e., chitosan and furfuryl alcohol were used as fillers for preparation of the polymer/C composites and C/C composites, respectively. The latter filler was carbonized, after filling a support and cross-linking, that transformed it into carbon rich coke. Figure 2 shows kinds of materials produced in our laboratory.

The polymer-carbon composite materials exhibit the chemical properties of the polymers used, whereas the stability of the pores against mechanical compression, thermal and chemical treatments is greatly enhanced. The resultant materials exhibiting surface properties of the fillers, as well as, electric conductivity and stiffness of the carbon framework, could provide new possibilities for advanced applications.

## 2. Monolithic carbon supports for the C/C and the polymer/C composites

### 2.1. Compressed expanded graphite

Graphite's structure consists with parallel hexagonal layers and because of above, the bond strength is much higher within the parallel layers than perpendicular to them. As layered solid, graphite may be exfoliated or "expanded" (exfoliation consists in separating the individual layers) by, at first, intercalation with acids and next by heating of the intercalated graphite, that results in a significant expansion of the material along the crystallographic c-axis. Expanded graphite is a promising material for a number of new purposes. Due to its performances in adsorption, raw EG was suggested as a new biomedical material and as a convenient way of sorption of high amounts of heavy hydrocarbons. The latter provides protection against heavy oil pollution after a tanker spill accident. Expanded graphite is commonly used in a compressed state (CEG). CEG combines an excellent thermal shock and chemical resistance. Because it has a low coefficient of surface friction and a low permeability, it is capable to operate successfully at temperatures from  $-200^{\circ}\text{C}$  up to  $+3500^{\circ}\text{C}$ . Highly porous monoliths based on slightly compressed EG are convenient supports for active carbon or polymer coatings and catalyst nanoparticles, both with application to environmental concerns [2, 9-11].

As it was stated previously, EG can be compressed very easily to form blocks with given shapes (Fig. 3), and with various densities depending on the compaction ratio. The resulting blocks are highly porous and present many interesting properties such as good electrical and thermal conductivities and mechanical strengths. All samples of monolithic CEG were made in our laboratory from EG provided by the Carbone-Lorraine Group (France), SGL Carbon (Germany) and ZEW Racibórz (Poland). The EG was poured into a vertical square tube (inner cross-section  $2 \times 2$  cm) and subsequently compressed by a close-fitting plunger. Depending on the initial mass of poured EG, consolidated parallelepiped blocks with various apparent densities ranging from 15 to  $272 \text{ kg/m}^3$  were obtained. These materials were characterized by high porosities in the range of 87.7-99.3%. Such

highly porous raw materials were thus easily impregnated by wetting fluids resulting in the C/C or the polymer/C composites [2, 4, 12].



Fig. 3. Monolithic blocks of CEG

## 2.2. Carbonized vascular plants

The increasing demand from consumers and industry for environmentally friendly and renewable polymers explain the great interest for macromolecules of natural origin as substitutes of synthetic polymers. The most recent efforts in the development of cleaner sustainable chemistry are being driven by a shift from petrochemical-based feedstocks toward biological materials and products based on them. New porous environmentally friendly carbon materials are prepared from hardwoods and softwoods or from plants different than trees via carbonizing them (Fig. 4) followed by impregnation with proper substances [6, 13, 14].

Wood precursors of infinite varieties are available providing different densities and pore morphologies, different levels of anisotropy, etc., and allowing a diversity of opportunities for material selection. The cellular anatomy of naturally grown plants provides an attractive template or matrix for the design of materials with hierarchically ordered structures that cannot be processed by conventional processing technologies. Heating of pieces of a plant stem to high temperatures of about 1000°C

increases carbon content and creates carbon structure of a given order [6, 8, 15]. Figure 5 shows a turbostratic structure of carbon performed by heating of constituents of wood: cellulose and lignin.

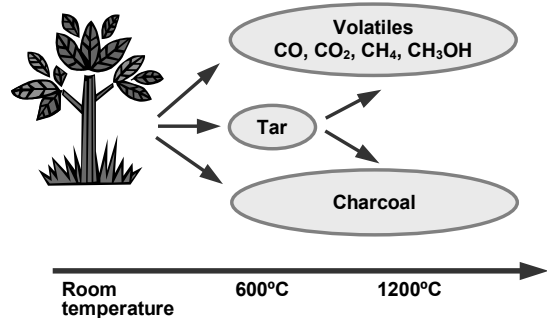


Fig. 4. Scheme showing process of carbonization of plant stem in the temperature range from room temperature up to 1200°C

The porous carbon materials could be used alone (active carbons, adsorbents) or for production of filtration systems, catalyst support structures and sensors. Practical implementations of wood-based materials such as electromagnetic shield materials, heater for floor heating, high-temperature absorbers and humidity sensors were also explored [5, 6, 8].

Materials produced from biomass feedstocks in technical processes also reduce the environmental burden. They consume fewer resources from eco-sphere, and reduce substances released to eco-sphere. Thus, searching of new materials based on the Nature sources, particularly based on the waste, is very important in respect to protection of natural environment. Biomass feedstocks such as dried stems of plants carbonized at proper temperatures are expected to be promising supports, as porous stiff skeletons, for the monolithic, biomorphous composites and as biotemplates for various biomorphous ceramics.

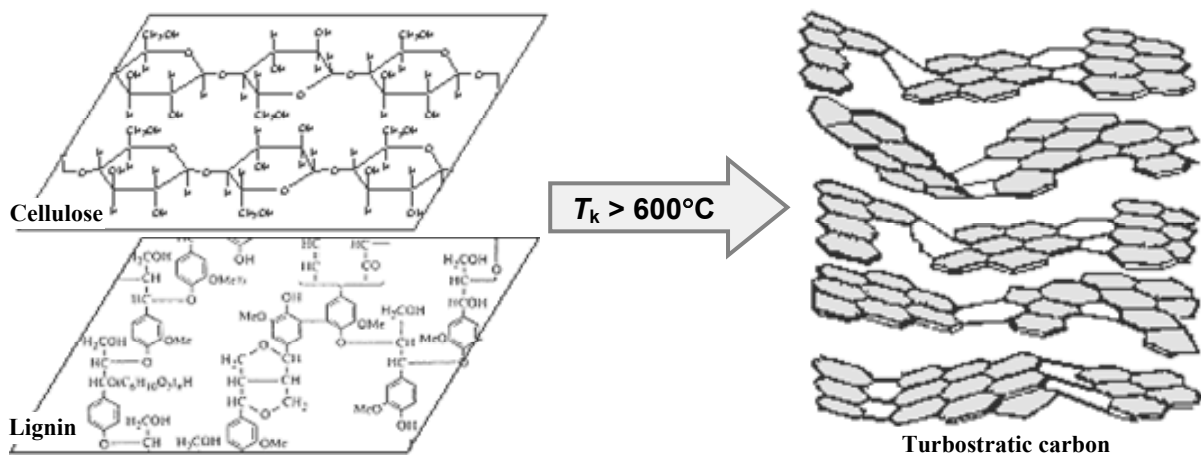


Fig. 5. Creation of turbostratic carbon structures from organic constituents of plants [8]

Most of the studies cited in the literature involved materials based on carbonized woods, which vegetate 20-30 years for softwoods and 40-60 years for hardwoods. It would be useful to prepare novel materials from varieties of plants with distinctly shorter period of renewal than that of long-growing plants. Amongst short-time renewable plants, mostly common bamboo was used for the manufacture of composites, while yucca (garden waste) was not applied for composites preparation. Figure 6 shows precursor for carbons produced from unusual genus of bamboo, i.e., solid iron bamboo (*Dendrocalamus strictus*) (SIB).

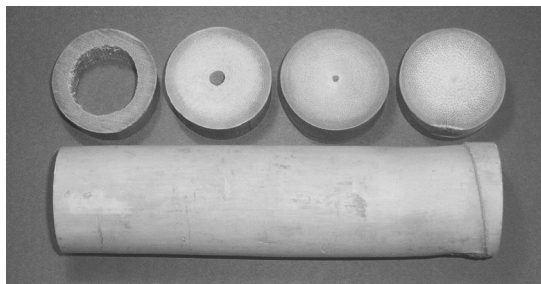


Fig. 6. Photo of pieces of *Dendrocalamus strictus* (SIB) cut along and perpendicularly to a stem. For comparison open ring of common bamboo (*Bambusa vulgaris*) is presented

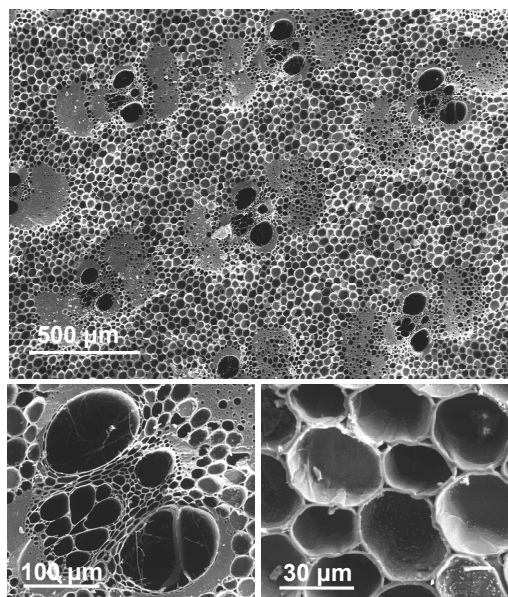


Fig. 7. The SEM image of cross section of the SIB stem carbonized at temperature 350°C

Cuboid pieces cut from woody stems of SIB and yucca (*Yucca flaccida*) with dimensions equal to for axial direction: 2-3 cm and for cross-section: (1-1.5)×(2-3) cm<sup>2</sup>, were used for carbonization. Block samples were heated in quartz furnace under a gas flow of nitrogen (about 0.1 l/min) in the temperature varying from 20°C to final temperature that was ranging from 300°C to 950°C. The rate of heating was constant for all final temperatures equal to

3°C/min. The samples were held for 1 h at desired temperature. Weight loss during the pyrolysis ranged from 50% to 70% for increasing heat-treatment temperature (HTT) from 300°C to 950°C. Carbon materials of lignocellulosic origin, carbonized under highly controlled conditions are marked by wide pore size distribution (the macro- and mesoporous structure) that reflects skeletons of original plants [7, 16, 17]. Figure 7 shows cross section of the SIB stem carbonized at temperature 350°C. It can be seen from this figure that pore system in this plant is differentiated distinctly. In order to make the pore structure of the carbonized plant more uniform, it is necessary to infiltrate it with carbonaceous polymers that are transformed during the carbonization into hard glassy carbon of textural and chemical reproducible properties.

### 2.3. Carbonized coal (coke)

Cokes are produced from a range of organic precursors, generally from coals. The most important cokes produced from coal are the hard metallurgical cokes used in blast furnaces. Cokes could be also applied to produce a wide variety of materials and, although the requirements of the coke differ according to the application, a coke of good strength characteristics is generally required in all processes. The properties of coke are influenced primarily by the nature of the parent material being carbonized. It is common practice to blend feedstock coals to produce a consistent coke, in particular, of high strength. Cokes used in our study were prepared from four single coals varying in caking propensities (weakly, moderately, strongly) and from their binary, as well as from ternary blends. They were carbonized at temperature of 950°C in a laboratory scale using the KARBOTEST apparatus [18]. Obtained cokes were highly porous materials of very strong skeleton. Despite high bulk porosity of ~50%, elastic modulus of the support ranged from 4 to 5 GPa.

## 3. Polymeric fillers for the C/C and the polymer/C composites

### 3.1. Furfuryl alcohol

One of the carbonaceous polymers frequently used for composite preparation is poly(furfuryl alcohol) (PFA). PFA is a cross-linked polymer that is synthesized from furfuryl alcohol (FA) derived from renewable resources. It is a very attractive precursor for carbon materials with ultramicropores. Owing to its unique physical and chemical properties PFA exhibits excellent processibility in a range of processes. PFA-derived carbons can be used as adsorbents, catalysts, and components for electrochemical and electric devices [12, 19]. However, materials usually applied as supports in the composites with PFA are not biodegradable and they need higher energy consumption in the processing than supports of natural origin. Carbonized plants of original structures combining different levels of porosities are expected to be promising supports for manufacturing hierarchical porous carbon/carbon composites with PFA.

### 3.2. Chitosan

Chitosan is the most important derivative of chitin, which is the second most important natural polymer in the world (after cellulose). It is obtained at an industrial scale by chemical deacetylation of crustacean chitin. Since it possesses many interesting properties, chitosan has found a number of different applications, e.g. in the production of food and cosmetics, in health care, biopharmaceutics, agriculture and to purge industrial pollution such as dyes, metal ions, odors, simple anionic molecules, etc. By coating metal or glassy carbon electrodes with this biopolymer it is possible to fabricate glucose biosensors. Bio-composites containing chitosan, with macroporous structures were suggested as suitable materials for tissue engineering, because chitosan has been reported to be biocompatible, safe and osteoconductive. The advantage of chitosan in such materials consists also in its biodegradability and its antibacterial activity [20-23]. The surface area of a chitosan film is important, since it is the area of contact between this polymer and the removed or monitored substance. Therefore, the deposition of a chitosan film on a highly porous support was admitted to be a good idea.

## 4. Techniques of preparation of the composites

### 4.1. Preparation of the C/C composites

The C/C composites were performed using three kinds of carbon porous supports: CEG, carbonized SIB or YF and coke with filler being PFA. Impregnation with furfuryl alcohol (99%) - a liquid of low viscosity - was performed in Epovac apparatus (Struers), in which the cuboid or cylinder blocks were soaked and submitted to three successive vacuum-pressure cycles. The samples, after taking out of the alcohol, were drained for a moment. Next, they were soaked in a solution of hydrochloric acid with a concentration of 2% for 5 or 6 h to initiate the polymerization step by an ionic mechanism. After complete impregnation, the materials were then first dried in air at room temperature for about 10 h and next in a drying oven at a slowly increasing temperature. Finally, they were kept over one night in the oven at a maximum temperature of 120°C. At this stage, the samples were dark and stiff composite materials.

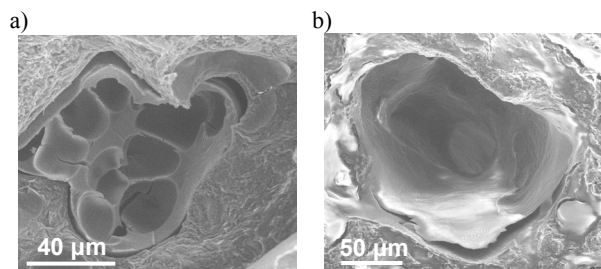


Fig. 8. The SEM image of the composites based on the coke from coal Jas-Mos as a support and PFA (a) and chitosan (b) as a filler

Next, the carbonization of the samples was performed in a quartz furnace under a flow of pure nitrogen. The temperature was slowly increased (5°C/min) until it reached a maximum at 550°C, then it was kept constant during 1 hour. The resultant materials were C/C composites (Fig. 8a, see also Fig. 9) for which a layer of the PFA coke was expected to coat the support all throughout the blocks [12, 24-27].

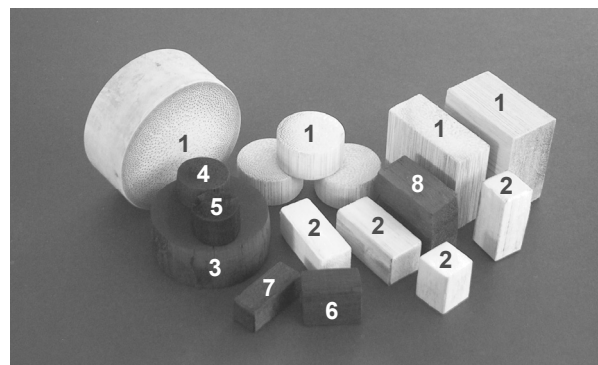


Fig. 9. Photo of raw SIB and YF, of carbonized SIB and YF, as well as of biomorphous C/C and polymer/C composites: 1 - raw SIB, 2 - raw YF, 3 - SIB600, 4 - SIB800, 5 - YF350, 6 - SIB600/Ch, 7 - YF550/Ch, 8 - SIB800/PFA. Number in names of the samples denotes the temperature of carbonization

The last step of the process, applied only to selected samples, was the activation of the composites using a steam or CO<sub>2</sub>. It was achieved in a quartz furnace, first flushed under nitrogen, which brought the materials to a temperature of 800°C for steam and of 900-950°C for gaseous CO<sub>2</sub> with the speed of the rise of temperature equal to 10°C/min. Activation medium was next passed throughout the system during a few hours at a given final temperature mentioned above [12, 28]. Activation generally increased the surface area of the composites from tens of m<sup>2</sup>/g to about 650-870 m<sup>2</sup>/g [12].

### 4.2. Preparation of the polymer/C composites

As in the case of the C/C composites, the polymer/C composites were performed using the same three kinds of carbon porous supports: CEG, carbonized SIB or YF and coke, but with the other filler being chitosan. Above porous monolithic supports were dried and infiltrated by water-acetic acid solution of chitosan from Sigma (0.25%) under vacuum (300 mbar) for 15 min. Next, the samples were dried at a temperature of 80°C until constant mass was reached. This procedure was repeated up to five times. After that the samples were cross-linked in 0.01 M glutaraldehyde solution for 2 h, dried at 80°C and rinsed, using ultrasounds, with 0.1 M NaOH solution to neutralize amino groups, followed by swilling out with distilled water to obtain neutral pH of the samples. The mass gain, Δm/m, of chitosan in the bio-composites ranged from about 1 up to 7.5 wt.% [29, 30]. Figure 9 shows

photo of the biomorphous composites and their precursors, while Fig.8b is the SEM image of the coke/chitosan composite. For all bio-composites, microscopic studies confirmed preservation of biomorphous cellular structure, characterizing porous supports obtained from carbonized plants. This can be seen from Fig. 10, that shows the SEM image of cross section of the biomorphous composite performed from yucca carbonized at 750°C and next covered by very thin film of chitosan (YF750/Ch).

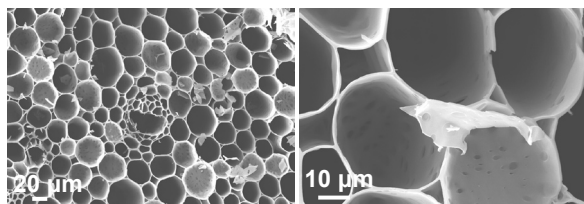


Fig. 10. The SEM image of cross section of the YF stem carbonized at 750°C and next covered by chitosan (YF750/Ch)

Additionally, the monolithic mica/expanded graphite nano-composites were prepared. EG of apparent density 2.6 kg·m<sup>-3</sup> supplied by Carbone Lorraine and mica powder (phlogopite) supplied by the French company LJC, were selected for the study. The samples of mica/EG composites were prepared as monolithic cubes of side 2 cm, by compressing more or less a mixture of EG and a fine powder of mica. Each composite was defined by the density of its graphite backbone and the weight percent of mica which was added. Four densities of the compressed EG backbone (CEG) were chosen as bases for the preparation of composites: 0.03, 0.05, 0.10 and 0.15 g cm<sup>-3</sup>. To the amount of EG particles required for reaching such densities in a cube of 8 cm<sup>3</sup>, a portion of powdery mica was added, and the mixture of both the powders was compressed in order to obtain the composite blocks, in the same way as pure EG cubes were prepared. The resultant monoliths exhibited layered structure of interesting anisotropic electrical properties.

## 5. Physicochemical characteristics of the C/C and the polymer/C composites

supports (CEG, carbonized plants, cokes), as well as of the resultant composites were characterized using various methods: the CHN analysis (carbon, hydrogen and nitrogen content), thermogravimetric analysis (TGA), helium gas densitometry, mercury porosimetry and the low temperature adsorption of N<sub>2</sub> gas, ultrasonic and electrical measurements, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), electron paramagnetic resonance spectroscopy (EPR) and observed with optical, scanning (SEM) and transmission (TEM) electronic microscopes. Block samples were used for the ultrasonic and the electrical measurements, helium gas densitometry studies and microscopic observations, while for the remaining methods the samples were ground to a powder of size suitable for a given technique. Details of the experiments were described in our

articles cited through all the text. The following parameters were determined for the samples studied: contents of carbon, hydrogen and nitrogen, true density (density of skeleton of porous sample), bulk porosity, the specific surface area,  $S_{BET}$  (calculated from the linear form of the Brunauer-Emmett-Teller equation), the mesopore and macropore size distribution, the velocity of longitudinal ultrasonic waves (frequency 100 kHz), dynamic elastic modulus and electrical conductivity measured parallel and perpendicularly to the stem/fibres, concentration of paramagnetic centres in both air and vacuum, weight loss vs. heating temperature, a kind and amount of functional groups present on internal surface (oxygen, carboxylic, phenolic, carbonyl, etc.), and height of the (002) peak on the XRD diffractograms. Selected data are shown in Table 1. They are ranged because of different the carbonization temperatures used and a direction in anisotropic medium: parallel or perpendicular to the stem/fibres.

Table 1.

The values of selected parameters of the materials studied: carbon content (C), bulk porosity (P), dynamic elastic modulus (E) and electrical conductivity ( $\sigma$ ).  $T_k$  denotes the final temperature of carbonization, ranged generally between 300 and 950°C

| Materials              | C (wt.%) | P (%) | E (GPa)    | $\sigma$ (S/cm)                     |
|------------------------|----------|-------|------------|-------------------------------------|
| <i>Supports</i>        |          |       |            |                                     |
| CEG                    | ~ 100    | 88-99 | $\leq 0.9$ | $0.2\text{-}5\cdot 10^2$            |
| SIBT <sub>k</sub>      | 72-82    | 73-86 | 1-4.7      | $3\cdot 10^9\text{-}6\cdot 10^{-1}$ |
| YFT <sub>k</sub>       | 71-81    | 88-90 | 0.2-2.4    | $6\cdot 10^9\text{-}3\cdot 10^{-1}$ |
| Coke                   | 98-99    | 53-56 | 4-5        | 1-3                                 |
| <i>Composites</i>      |          |       |            |                                     |
| SIBT <sub>k</sub> /PFA | 86-87    | 73-81 | 2-5        | $2\cdot 10^5\text{-}1$              |
| YFT <sub>k</sub> /PFA  | ~ 90     | 60-74 | 2.4-2.7    | $2\cdot 10^7\text{-}4\cdot 10^{-1}$ |
| SIBT <sub>k</sub> /Ch  | 69-83    | 70-77 | 1.5-5      | $3\cdot 10^8\text{-}9\cdot 10^{-1}$ |
| YFT <sub>k</sub> /Ch   | 67-83    | 88-91 | 0.4-2      | $1\cdot 10^8\text{-}4\cdot 10^{-1}$ |

The C/C and the polymer/C composites were found to be materials: light with apparent density ranging from about 0.1 g/cm<sup>3</sup> to about 0.5 g/cm<sup>3</sup>, very porous (up to 90%), thermo-resistant (in oxygen-absent atmosphere) with stiff (modulus of several GPa), hierarchically ordered structures. These eco-friendly composites were found to be monoliths comprising a backbone, i.e. carbonized plant or compressed expanded graphite skeleton, coated with a thin layer of a filler - carbonized cross-linked PFA or cross-linked chitosan. Electrical conductivity of the composites was found to be strongly dependent on the electrical properties of the support. Covering internal surface of the conductive carbonized plant or CEG with a thin layer of the filler, being an insulator, does not change drastically electrical resistance of the resultant composite. This new kind of monolithic porous materials could be of great interest as adsorbents or as catalyst supports.

## 6. Application of obtained materials

It is well-known, that the PFA-derived carbons can be used as adsorbents, industrial catalysts supports and components for electrochemical and electric devices [12, 32-34]. The monolithic porous C/C composites, produced using carbon backbone from both CEG and carbonized plants with PFA as a filler, can be used

in these kinds of applications, especially for removal of different pollutants from water, for purification of waste solutions, for separation and concentration of radioactive isotopes, for production and analysis of high purity substances, etc. Except of the materials having the lowest densities, the conductivities of the C/C composites of type of CEG/PFA have the same order of magnitude as that of pure CEG (about tens of S/cm). Thus, these materials could be electrically regenerable adsorbents [12].

On the other hand, more and more attention is dedicated to elaborate an eco-friendly composite materials. As it was stated earlier, chitosan seems to be very promising in that field, because it can replace synthetic polymers. A lot of research was carried out to elaborate macroporous composites based on chitosan, that were suggested as suitable materials for various applications, especially in medicine as e.g. glucose sensors, as well as in tissue engineering. Biocompatibility, antibacterial activity and biodegradability are very important in medical uses [20]. Generally, biomorphous carbon materials are expected to be appropriate for preparation: adsorbents/absorbents, catalysts supports at high temperatures, sensors, filters, and of course, medical implant structures, etc. [35-41]. In the case of monolithic polymer/C composites with carbonized plant covered by thin film of chitosan, it is very important that both the support and the filler are made using only natural biological precursors.

The first studies on application of our materials were made in the field of the As(III) adsorption and of the oximetric probes for medicine.

Arsenic is one of the most dangerous pollutants, which is introduced into natural waters by geochemical reactions, by agricultural use of arsenic pesticides, herbicides, fertilizers, by industrial waste discharge, from coal fired thermal power plants, from petroleum refining and from ceramic industries [35]. In our works two kinds of materials: solid iron bamboo carbonized at 750°C, next activated with steam and the bio-composite from yucca carbonized at 750°C, next covered by chitosan, were utilized for the removal of the As(III) ions dissolved in water with concentrations ranging between 5 and 20 mg·L<sup>-1</sup> [8, 35].

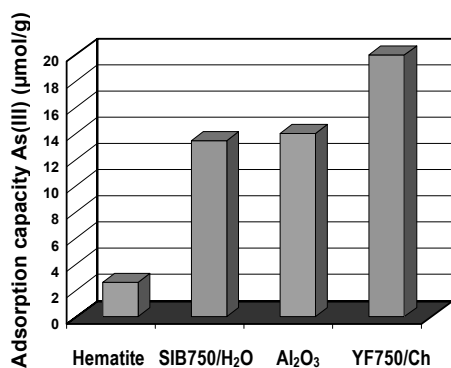


Fig. 11. Comparison of the adsorption capacity of As(III) from water determined using our materials: SIB750H<sub>2</sub>O and YF750/Ch with that of commercial adsorbents: hematite and Al<sub>2</sub>O<sub>3</sub>

The results are shown in Fig. 11. It can be seen from this figure that eco-friendly and biodegradable materials based on natural precursors were found to be distinctly more effective adsorbents than those commercial, such as hematite and Al<sub>2</sub>O<sub>3</sub>.

Carbon materials could be used as oximetric probes for biological systems, because they contain sufficient amount of paramagnetic centres, if they are carbonized at high enough temperatures [42, 43]. High concentration of spins indicates susceptibility of materials to oxygen. Oximetry is a very important technique to register formation of singlet oxygen during photodynamic therapy of tumor cells, that generates intensive excitation of oxygen molecules to singlet state [44]. Singlet oxygen formation in cells is accompanied by decrease of amplitude of EPR lines registered in a paramagnetic material. New oximetric probes including carbon materials are intensively searched. Both bamboo and yucca carbonized at various temperatures ranging from 550 to 950°C were studied by EPR. It was stated that amplitudes of the EPR lines of all the carbonized plant samples registered in air (containing oxygen) were distinctly lower than amplitudes of spectra measured in vacuum (Fig. 12). This effect increases with degree of vacuum: the lower the oxygen content, the higher the EPR amplitude. Quasi-chemical bonds between carbon material and oxygen molecules are responsible for this effect. Changes in the EPR spectra of samples studied may be applied in medicine for determination of oxygen content in cells differentiated by disease. Because of strong resonance signals, bamboo and yucca carbonized at 550°C were proposed as oximetric probes [42].

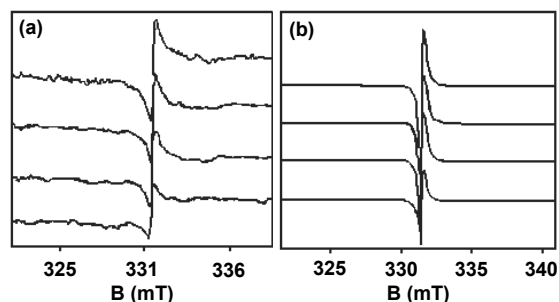


Fig. 12. The EPR spectra in air (a) and in vacuum (b) of yucca carbonized at 650°C with various values of microwave power attenuation

Carbonized plants alone, without covering by polymeric fillers, can be utilized as humidity sensors. Usually, for humidity sensors various ceramics are used. When a certain voltage is applied to the ceramics humidity sensor, an electrical resistance exponentially alters with a relative humidity, whereby a value of the relative humidity can be detected on the basis of the electrical resistance [45, 46]. However, there is a certain problem: most of the ceramic humidity sensors have non-linear characteristics. This problem does not exist in the case of carbonized plants. Figure 13 shows the relationship between relative humidity and resistance measured for the sample of wood prepared at 650°C. The data were obtained by Kasai et al. [45]. It can be seen from Fig. 13 that the resistance decreased linearly as the humidity increased from 40% to 80%. What is more, the hysteresis was found to be small for this humidity range. Therefore some solutions of humidity sensors based on woodceramics (WCS), i.e., carbonized woods were proposed [46]. Additional advantage of using woodceramics is that they are inexpensive, excellent in heat resistance and very accurate. Humidity sensors can be used not only to measure a humidity in an atmosphere, but also to

automatically control humidifiers, dehumidifiers, air-conditioners for humidity adjustment and the like. Figure 14 shows the structure of the experimental WCS humidity sensor proposed by Kasai et al. [45].

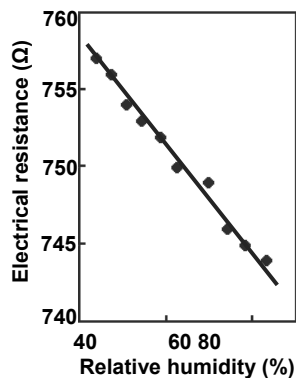


Fig. 13. The relationship between relative humidity and electrical resistance for the specimen of woodceramics prepared at 650°C

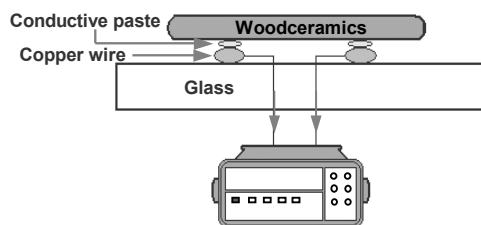


Fig. 14. Structure of woodceramics humidity sensor

## 7. Conclusions

Composites produced using monolithic carbon supports of high porosity and two polymers: furfuryl alcohol and chitosan were an objective of the studies in our laboratory. These materials were found to be light with apparent density lower than 0.5 g/cm<sup>3</sup>, very porous (up to 90%), with stiff hierarchically ordered structure of dynamic elastic modulus of order of several GPa. The first studies on practical uses showed that they are better adsorbents than commercial ones, and they have potential to be good oximetric probes in medicine. It is important that C/C and polymer/C composites were performed using biopolymers, that are abundant, renewable, biodegradable, and recyclable.

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