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Development of monolithic eco-composites from carbonized blocks of solid iron bamboo (*Dendrocalamus strictus*) by impregnation with furfuryl alcohol

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ABSTRACT

The purpose of this work was to manufacture the porous biomorphous composite using carbonized shapes cut from solid stem of solid iron bamboo, *Dendrocalamus strictus*, as a monolithic support. Bamboo carbonized at 800 °C was next infiltrated with liquid filler – furfuryl alcohol. After the polymerization and cross-linking of the filler, the shapes were carbonized again to obtain carbon/carbon composite. TGA method was used to investigate the thermal decomposition of the resulting composite as well as of the raw and carbonized bamboo. The ultrasonic measurements, optical microscopy observations, the adsorption of N_2 at −196 °C and mercury porosimetry were applied to characterize the structure of the investigated materials. The obtained composite was found to be highly porous (over 80%), thermo-resistant in inert atmosphere (up to 940 °C). It possessed stiff hierarchically ordered pore structure with elastic moduli >4 GPa along the stem, and >1 GPa perpendicularly to the stem. Furthermore, the layer of carbon from the polymer coated the support accurately and did not affect the shape of the monolithic pieces of carbonized bamboo. The resulting composite possessed also more uniform, mesoporous structure than the support.

1. Introduction

As a result of the increasing demand for environmental protection, new materials and processes have been developed in order to reduce or eliminate the use and generation of hazardous substances (Ashori, 2008; Sud et al., 2008). Renewable feedstock such as wood, bamboo, agricultural waste etc., allows to obtain new advanced materials. Cellular anatomy of plants provides an attractive template for the design of materials with hierarchically ordered structures that cannot be processed by conventional technologies (Byrne and Nagle, 1997).

During highly controlled carbonization of plants it is possible to produce porous carbons with the structure that retains all of the anatomical features of the precursor. Such materials can be used as bio-templates to produce porous biomorphic ceramics (Greil, 2001). They are achieved thanks to the conversion of wood caused by different infiltration reactions and subsequently by calcination or sintering at high temperatures. They replicate the morphology of native materials and exhibit a unique, uniaxially oriented pore structure. Another kinds of material that can be produced from carbonized or raw wood are composites. They are obtained by polymer infiltration into carbonized wood monolith (support) or plant fibers to form carbon/polymer composites. If a high char yielding polymer is used, the second carbonization gives a carbon/carbon composite. Biomorphous carbon materials are expected to be appropriate for various applications: adsorbents/absorbents, catalysts supports at high temperatures, sensors, filters, as well as for medical implant structures etc. (Li et al., 2006).

So far for the preparation of biocomposites, bamboo has been frequently used as a source of fibers or powders (Thwe and Liao, 2003; Wu et al., 2008), which are natural fillers of polymer matrices. Polymers/bamboo fiber biocomposites with bamboo fiber content reaching up to 50% were found to be strong with Young's modulus about 2–3.5 GPa (Lee and Wang, 2006). Composites containing carbonized block bamboo or grains as a support and a polymer as a filler are rather rare (Chuang et al., 2008).

Bamboo is a member of the grass family. It contains highly aligned long cellulosic fibers that make up a strong woody, stem (culm). One of the most important advantages of bamboo is a very short time of growing in comparison with other plants, especially with trees, because bamboo needs only 3–5 years to reach maturity. Among various kinds of bamboo *Dendrocalamus strictus*, known as "iron" or "male" bamboo, is a especial genus because of its unusual properties (Krzesińska and Zachariasz, 2007; Krzesińska et al.,

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2008). Native to India, it is unique in that the culm is thick-walled, often solid. Probably it is the strongest bamboo in the world. Three years are sufficient to get hard, insect-resistant material with a homogeneous profile and homogeneous vessel distribution, actually a more homogeneous structure than that of trees. Unlike the common bamboo possessing hollow culm, solid iron bamboo (SIB) can be cut into rectangular or square shapes.

Carbon precursors 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 (Laszlo et al., 2005; Mizuta et al., 2004). 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 (Garcia-Bordeje et al., 2006).

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 (Celzard et al., 2002; Wang and Yao, 2006). 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 promising supports for manufacturing hierarchical porous carbon/carbon composites with PFA.

There is not any detailed and original previous research reporting properties of a especial genus of bamboo, i.e., solid iron bamboo, except of our previous two papers (Krzesińska and Zachariasz, 2007; Krzesińska et al., 2008). We reported the thermal decomposition of SIB and the effect of pyrolysis temperature on the physical properties of monolithic carbons derived from SIB. Current work is continuation of studies described in articles mentioned above. The aim of this study was to prepare the novel biomorphous composite on the basis of new monolithic porous carbon material developed from solid, very strong culms of SIB and hard glassy carbon derived from poly(furfuryl alcohol) during carbonization, and to describe the composite's as well as the precursor's properties.

2. Experimental

Cuboid pieces cut from woody stems with sides equal to: for axial direction 2–3 cm, for radial direction 1–1.5 cm and for tangential direction: 2.5–3.5 cm were used for pyrolysis. Block samples were heated 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 900 °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 900 °C. Porous carbons obtained at the pyrolysis temperature equal to 800 °C were chosen for further studies. The block samples of SIB carbonized previously at 800 °C, were impregnated under vacuum by furfuryl alcohol (99%) in Epovac apparatus. Next, the samples were dried in the air for an hour and soaked in the solution of hydrochloric acid (2%) for 5 h. After the impregnation and polymerization the samples were dried in the air for an hour and then in the dryer in the temperature range 80–120 °C for 7 h. The resultant composites were carbonized under nitrogen with the constant heating rate of 3 °C/min to the temperature 550 °C and kept at this temperature for an hour.

Monolithic block samples of SIB, raw and carbonized, as well as of the resultant composite were characterized using various methods: elemental analysis, TGA, helium gas densitometry, a mercury porosimetry and the low temperature adsorption of N_2 gas, the ultrasonic measurements, and observed with the optical microscope. Block samples were used for the ultrasonic measurements, helium gas densitometry studies and microscopic observations, while for the CHN analysis, the TGA and the pore size distribution studies, the samples were ground to powder. The CHN analysis (carbon, hydrogen and nitrogen content) was made with the Perkin Elmer 2400 Series II CHNS/O System.

The TGA technique was applied for the thermal characterization. Thermogravimetric studies were carried out with a thermogravimetric analyser TGA type Q–1500, MOM Budapest, as in the case of carbonization, in pure nitrogen, with a flow rate of 10 l/h. Samples were heated from temperature 20 °C to 940 °C at a heating rate of 10 °C/min.

Both apparent and the true densities were measured to determine the bulk porosity of samples. The true density was measured using helium gas displacement pycnometer type 1305 Micromeritics®. The bulk porosity of the samples was calculated using the expression:

$$P(\%) = \frac{\rho_{\text{true}} - \rho_{\text{app}}}{\rho_{\text{true}}} \cdot 100 \qquad (1)$$

where P is a bulk porosity, ρ_{true} and ρ_{app} are true and apparent densities of a sample, respectively. The mesopore size distribution of the materials was measured by means of the adsorptive method. The adsorption of N_2 at liquid nitrogen temperature was achieved on small samples into a standard volumetric apparatus ASAP 2000 (Micromeritics®). Every sample was degassed in a vacuum under a pressure about 5 μm Hg, at temperature 140 °C for 120 h. The adsorption/desorption isotherms of nitrogen were determined point-to-point by discontinuous introduction of adsorbate into a sample holder. A number of adsorption and desorption points were performed for relative pressures in the range 0.05–0.99. The pore (mesopore) size distribution was calculated in the standard manner using the Barrett–Joyner–Halenda method. Investigations of larger pores were made using a mercury porosimetry by means of an apparatus AUTOPORE 9220, Micromeritics®. The amounts of mercury introduced into pores of previously degassed material were determined for the serial previously selected pressures attaining up to 35 MPa. The pore (macropore) size distribution was calculated using the Washburn equation.

The velocity of longitudinal ultrasonic waves at a frequency of 100 kHz was measured along parallel (axial direction) and perpendicular (radial and tangential directions) to the stem/fibre directions, using an ultrasonic tester (Tester CT1, UNIPAN-ULTRASONIC, Poland). Details of an ultrasonic method are described in our previously published papers (Krzesińska et al., 2006; Krzesińska and Zachariasz, 2007). Ultrasonic velocities (v_{ax}, v_{tan} and v_{rad}) were measured for SIB, before and after carbonization, as well as for the resultant composite. Ultrasonic velocities and apparent densities, ρ_{app}, were used for the determination of the dynamic elastic moduli E_{ax}, E_{tan} and E_{rad} as follows:

$$E_i = \rho_{\text{app}} \cdot v_i^2 \qquad i \equiv \text{ax}, \text{tan}, \text{rad} \qquad (2)$$

The structures of raw and the carbonized SIB, as well as of the composite were observed for the set of cuboid samples along axis of a stem and perpendicularly to it, using light microscope LEICA, with magnification up to 500x.

3. Results and discussion

The studies of the thermal decomposition of SIB raw and carbonized at 800 °C as well as of the composite, were carried out in