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The physical properties of biomorphous composite derived by infiltration of furfuryl alcohol into carbonized, monolithic blocks of Yucca flaccida

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Abstract. The block samples of yucca (Yucca flaccida) carbonized at temperature 350°C were impregnated under vacuum by furfuryl alcohol, which was next polymerized by solution of hydrochloric acid and cross-linked. The impregnated samples of carbonized plant were heat-treated again at 550°C to carbonize the filler. The resultant composites were characterized using a helium gas densitometry, the ultrasonic measurements, and observed with light microscope, as well as with SEM. Various physical parameters: the true density, the bulk porosity, the longitudinal ultrasonic wave velocity and elastic anisotropy were determined. The thermal decomposition of carbonized yucca modified by polyfurfuryl alcohol was investigated at temperature ranging from 20 to 940°C using thermogravimetric analysis (TGA).

1. Introduction
Plant precursors carbonized at various temperatures are supposed to be one of the best biomorphous supports to produce monolithic, eco-friendly composites, which can be used for very wide range of applications (activated carbons, adsorbents, catalyst supports, sensors etc.) [1−4]. The cellular anatomy of naturally grown plants provide an attractive template for the design of materials with hierarchically ordered structures on different length scales that cannot be processed by conventional processing technologies [5].

In our previously published articles [6,7] we presented composite materials made of compressed expanded graphite as a support and polyfurfuryl alcohol as a filler. The resultant materials were monoliths comprising a graphite backbone coated by a thin layer of active carbon. The electrical conductivity and the dynamic elastic moduli were measured on each kind of material, namely before and after carbonization, and finally after activation. Their conductive and elastic properties were shown to be very good. Hence, the materials were expected to have fair thermal conductivities, to be electrically regenerable (application as adsorbents) and to have an interesting life time (application as catalyst supports). It would be useful to exchange a graphite support for an ecological support, i.e., for carbonized plant, remaining polyfurfuryl alcohol as a filler.

The aim of this work was to prepare the monolithic biomorphous composite using the carbonization product derived from yucca (Yucca flaccida) as a support and polyfurfuryl alcohol as a filler, and to study the physical properties of this composite.

2. Experimental
Monolithic porous carbon materials from the woody stems of yucca were produced using slow pyrolysis at the temperatures 300–950°C [8]. Porous carbons obtained at the pyrolysis temperature equal to 350°C were chosen to the further studies. The block samples of carbonized yucca 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 hours. 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 hours. The resultant composites were carbonized at 550°C, under nitrogen. They were heated with the constant heating rate of 3º/min and kept at this temperature for an hour. Fig. 1 shows samples of initial yucca, carbonized at 350°C and the composite.

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For the thermal characterization of the composite, the TGA technique was applied. Thermogravimetric studies were carried out with a thermogravimetric analyser TGA type Q–1500, MOM Budapest (Hungary), in pure nitrogen with a flow rate of 10 l/h. Samples of about 100 mg of powdered composite were placed in a platinum crucible and they were heated from temperature 20°C to 940°C at a heating rate of 10°C/min.

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

\[ P(\%) = \left(1 - \frac{\rho_{\text{app}}}{\rho_{\text{true}}} \right) \cdot 100\% \]

where \( P \) is a bulk porosity, \( \rho_{\text{true}} \) and \( \rho_{\text{app}} \) are true and apparent densities of a sample, respectively. An apparent density was calculated from volume of a sample and its weight.

The velocity of the longitudinal ultrasonic wave, \( v \), at a frequency of 100 kHz was measured along axial and radial directions, i.e., parallel and perpendicularly to the stem/fibre direction, respectively, using an ultrasonic tester (Tester CT1, UNIPAN-ULTRASONIC, Poland). Details of ultrasonic measurements are described in our previously published papers [9,10]. Ultrasonic velocity was measured along both axial and radial directions for yucca, before and after carbonization, as well as for the resultant composite. Elastic anisotropy was determined as a relation \( v_{\text{ax}}/v_{\text{rad}} \).

The structure of samples studied was observed using scanning electron microscope (SEM), Zeiss, Germany, with magnification up to 5000x. Before the observation with light microscope, samples were polished. After light microscope observation the same samples were evaporated with gold and studied by means of SEM.

3. Results and discussion

It is known from our previously published article [9], that strong EPR signals were characteristic for the yucca thermally decomposed at lower temperature (550°C), while yucca heated to higher temperature (950°C) was described by weak EPR lines with high level of noise. High concentration of paramagnetic centres (~10^20 spin/g) resulted from breaking of chemical bonds during the thermal decomposition of plants was registered in the yucca heated to 550°C. Heating to 950°C quenched paramagnetic centres, i.e., concentration of paramagnetic centres decreased from ~10^20 to ~10^17 spin/g. This means that for the composite preparation, samples carbonized at lower temperatures are more suitable because of high number of not-saturated bonds.

Figure 2 shows the DTG curve (the first derivative of a function of weight loss plotted vs. temperature) for raw yucca and the composite. It can be seen from this figure, that the yucca was thermally decomposed at the temperature range ~270–350°C with distinct loss of weight at 330°C. Thus, the samples carbonized at 350°C were chosen to the further studies, because they were recognized as suitable for the composite preparation.
Figure 3 shows the true density, i.e., the density of continuous matrix of porous blocks of yucca raw, carbonized and the composite. The $\rho_{\text{true}}$ value of yucca carbonized at 350°C is close to 2 g/cm$^3$, i.e., it is slightly lower than the density of graphite (2.25 g/cm$^3$). The $\rho_{\text{true}}$ value of the composite is lower than that of its support. This means that the support is covered compactly by a layer of the cross-linked filler, lighter than carbonized yucca matrix. Figure 4 shows the bulk porosity of initial plant stem, support and the biomorphous composite. The empty space in highly porous carbonized yucca was filled partly by filler – furfuryl alcohol. This explains the reduction of the bulk porosity in comparison with the highly porous carbon support. All materials studied are very porous with the $P$ value ranging from about 73 up to 90%.

Figure 5 shows the ultrasonic wave velocity measured along basic directions of a sample, i.e., along axial and radial directions in yucca raw, the carbonized and in the composite. The acoustic parameter determined along axial direction is distinctly higher than that along direction in the plane perpendicular to the stem axis. It is clear, because strong fibers of yucca are aligned parallel to the stem axis. It is known that the ultrasonic wave velocity propagated through porous medium depends on the bulk porosity (decreases with increasing porosity), as well as on stiffness of continuous matrix (increases with increasing the matrix stiffness). The carbonized yucca is the most porous medium with comparison with raw material (plant) and the composite. Therefore, the lowest value of the ultrasonic wave velocity for this material is not surprising. Thus, in the case of the materials studied, the bulk porosity is more important parameter, affecting the stiffness of medium, than the stiff properties of solid matrix. The ultrasonic velocity measured along radial direction in the composite is the highest among the materials studied.

Figure 2: The thermogram (DTG = $dw/dT$; where $w$ – weight loss (wt.%), $T$ – temperature (°C)) of raw yucca and the composite, determined using thermogravimetric analysis (TGA); notation: 1 – the composite, 2 – raw yucca

Figure 3: The true density of yucca raw, carbonized and the composite

Figure 4: The bulk porosity of yucca raw, carbonized and the composite
Figure 6 shows the changes of elastic anisotropy of structure of materials studied, from initial plant to the resultant composite. High decrease of the value of $v_{ax}/v_{rad}$ observed for the composite, is caused by filling of pores.

Similarly, as in the case of composites made of compressed expanded graphite as a support and polyfurfuryl alcohol as a filler, the resultant eco-composites were found to be monoliths comprising a backbone – carbonized yucca tissue coated by a thin layer of active carbon. This activity is expected to be not sufficient. The next step is activation using CO$_2$ or water vapor. These studies will be continued.

Figure 7 shows transverse and longitudinal sections of the support produced from yucca carbonized at 350°C. It can be seen from this figure that the natural plant tissue was not destroyed during heating. Fibrils aligned along the stem axis are characterized by various diameters. Yucca is very useful support for eco-composites because of great empty space accessible for filler.

Figure 5: The ultrasonic wave velocity determined along basic directions: axial (high columns) and radial (lower columns) in raw yucca, carbonized and in the composite

Figure 6: Elastic anisotropy determined as $v_{ax}/v_{rad}$ for yucca raw, carbonized and the composite

The thermogravimetric studies of the composite (Figure 2) did not reveal any decomposition of this material up to 940°C, except of very low weight loss around 690°C (a wide, not deep minimum in the DTG curve). It is evident that the composite is thermo-resistant in a wide range of the temperatures, although it was derived from the product of low temperature carbonization of yucca. This makes the composite suitable for application at high temperatures.
4. Conclusions
The biomorphous composites, derived by infiltration of furfuryl alcohol into carbonized at 350°C monolithic blocks of yucca, were presented in this study. They were found to be very porous, thermo-resistant carbon materials with very stiff, hierarchically ordered structure. Furfuryl alcohol was found to be filler compactly adhered to the ecological support. These preliminary studies will be continued.

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