



Obtaining of biomorphic composites based on carbon materials

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Abstract

Aim of this paper is to present the properties of carbon preforms for the production of biomorphic composites. Carbon samples were obtained through pyrolysis of paulownia wood, replicating the microstructure of the cellulosic precursor. Many characterization methods such as Raman Spectroscopy, light microscopy, hardness tests and pore size analyzer detection were used to investigate the microstructure of the product as well as the pore size of carbon samples. Obtained results showed that the parts of early or late wood template play an important role in the pore size, specific surface area and pore volume of the product. This review aims to be a comprehensive description of the development of carbon chars: from wood templates and their microstructure to potential applications of biomorphic materials.

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1. Introduction

Cleaner production represents a program based on continuous strategies applied to a more sustainable use of materials and energy, minimizing waste and pollution. The use of natural materials and the subsequent modification of their properties often allows for the replacement of materials whose impact on the environment is strongly unfavorable. Wood is an excellent example of natural material, because it is obtained from controlled resources, might be used as a fuel, might be used as a material itself or can be part of composite material and almost do not generate any waste. In modern materials science, biomorphic materials are becoming more important, which is confirmed by numerous publications and research. Research on wood or coal materials is becoming more and more popular due to the high availability of this raw material. An example of the modern use of natural materials can be research conducted by scientists from National Tsing Hua University in Taiwan, who carried out synthesis of hierarchically porous structured CaCO_3 and TiO_2 replicas by sol-gel method using lotus root template. The conclusions of this work showed that the synthesized materials with hierarchical biomorphic structures may have great potential for purification applications due to their large specific surface area, photocatalytic properties, and high adsorption rate (Chen et al., 2016). Another research team from Anhui Agricultural University in China carried out

synthesis of Biomorphic Charcoal/ TiO_2 Composites from Moso Bamboo Templates for Absorbing Microwave. They discovered that the C/TiO_2 sintered exhibited low geometrical density, good thermostability and favorable microwave absorptive properties (Qian, 2016). In Chinese Academy of Sciences the biomorphic cellular $\text{C}/\text{SiC-ZrC}$ composite ceramics from wood was fabricated and characterized. Carbon preforms as a result of wood pyrolysis are an excellent material for the preparation of biomorphic composites.

2. Experimental

To produce samples wood from Paulownia Clone in Vitro 112 also known as Oxytree was used. The material was cut out from the cross section of the wood trunk in the cylindrical form with an average dimension of 26.00 mm diameter and 11.7mm height. The wood samples were dried to remove the free water contained in the pores of the wood material. In order to reduce moisture the drying process ran at 80°C for 2 hours and 120°C for 12 hours. In the next step, the dry samples were subjected to a pyrolysis process in 600°C for 12 hours. The heating was carried out from 25°C at a rate of 3 °C/ min to the final temperature in non-oxygen atmosphere in furnace PRC 80x460/170 produced by Czylok Company. After heating the samples were cooled slowly in the furnace for two hours. The samples were sanded and polished per-

pendicular surfaces to the direction of the wood trunk to expose the porous cell structure. To avoid clogging of the pores, grinding was carried out in a stream of distilled water. In addition, the grinding samples were placed in an ultrasonic washer and sonicated in distilled water for 15 min in 20°C to completely get rid of the loose carbon fractions.

The investigation of the obtained preform materials were performed using light microscopy for microstructure and pore size determination, Raman spectroscopy for microstructure and chemical composition determination along with hardness tests. Optical microscopy studies were carried out using a Zeiss Observer.1Zm with the Dark field and Circular Differential Interference Contrast observation methods and using metallograph microscope MEF 4A produced by Leica. The Raman spectroscopy study was performed using the Ranishaw Raman microscope with a laser length of 514 nm in order to identify the carbide phases. The hardness tests were performed using hardness tester Zwick 3106 produced by Zwick/Roell company. The hardness tests were performed with a 1 kg load dwell time of 10 s and repeated 10 times for areas of late and early wood. The obtained results were averaged.

3. Results and discussion

Wood materials is natural composite materials of complex hierarchical cellular structure (Gibson, 1992). Wood component which are hardwood and softwood are comprised of longitudinal cells with square similar cross-section. Elongated wood cells in the form of vessels called tracheas are arranged in the direction of the growth of the trunk. The size of these cells and their distribution varies significantly among different species of wood. In the case of softwood cells structures is less complicated anatomically with significant participation of ordered longitudinal tracheid (Greil, 2001). Some of the wood samples were cut and polished to expose the structure of early and late tissue before pyrolysis process to determine the structure of wood, its porosity and the difference in the construction of resinous vessels (Fig. 1). There is a visible border between early and late wood, resulting from the rate of tree growth in a given period of time. Growth rings result from the difference in density between the early wood (spring wood) and the late wood (summer wood). What is visible in the picture, early wood is less dense because the cells are significantly larger and their walls are thinner. In spite of fact, that the transition of early wood to late wood within a growth ring might be obscure, the demarcation between the contiguous late wood of one ring and the early wood of the next ring is clear. Diffuse-porous wood occurs when the size of the vessels in a growth ring are quite uniform and evenly distributed. Ring-porous wood occurs when the pores of the early wood are distinctly larger than those of the late wood (Worbes, 1999).

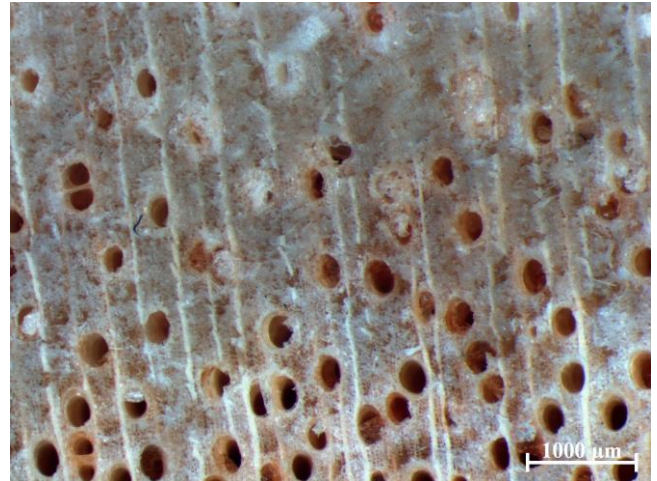


Fig. 1. Structure of wood before pyrolysis, view from the front

As a result of the pyrolysis process in 600°C, biomorphic preforms were obtained. The aim of the carbonization process is decomposition of wood into pure coal with the participation of other carbon compounds (tar substances or volatile hydrocarbons). The average sample weight before pyrolysis is 1.35g and average weight after is 0.38g. There was also a reduction in the dimensions of the samples that were at the beginning of 26.00 mm diameter and 11.7mm height and after the pyrolysis 20.9 mm diameter and 10.4mm height. Weight loss at 72 wt% and dimensional reduction was caused by the decomposition of organic wood components and the removal of water. In the presence of water contained in the porous structure of the wood, as a result of high temperature pyrolysis, the carbon forms volatile aliphatic and aromatic hydrocarbons as well as carbon dioxide, which results in the loss of sample mass. Purification and polishing of samples revealed the porous cellular structure of wood (Fig. 2).

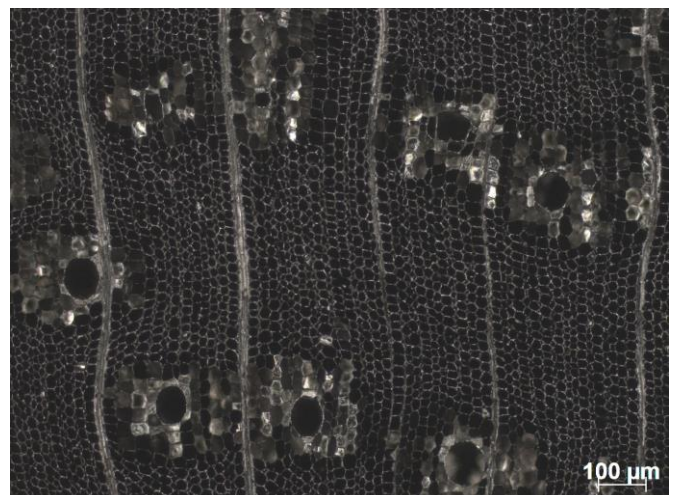


Fig. 2. Structure of carbonized samples view from the front. Layer system derived from early and late wood

The front surface of the pyrolyzed samples, which is visible in the pictures obtained by light microscopy, shows a stratified pore system, representing the annual growth of wood.

Visible layers in the form of light (compacted) and dark layers correspond to the system of increments of respectively late and early wood.

Pore-derived wood cells exhibit a near circular shape with average dimensions of $290.5\mu\text{m}$ for early wood and $35,8\mu\text{m}$ for late wood. The structure of biocarbon char consists of a parallel arrangement of open vessels with a length of about $200\mu\text{m}$, connected to each other by circular pits (Fig. 3). Visible layers in the form of light (compacted) and dark layers correspond to the system of increments of respectively late and early wood. Wood parts that grow in the early season have a greater diameter and are characterised by lighter weight in comparison to late wood. The width of individual layers is heterogeneous, as well as the exact parallelism of the layer system is not maintained.

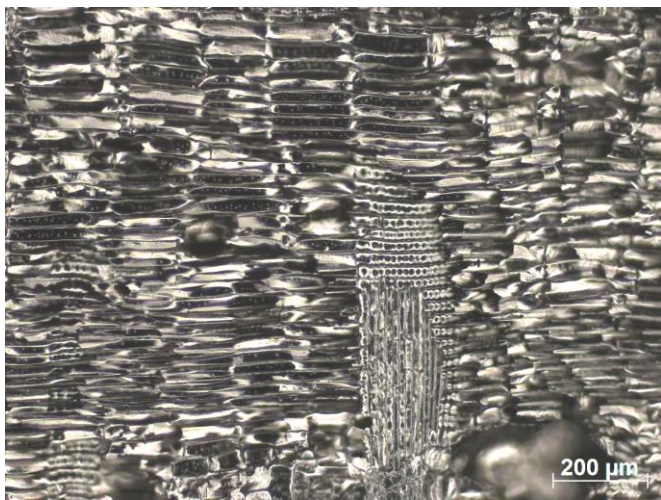


Fig. 3. Structure of carbonized samples view from the cross-section, irregular cellular structures

In order to check the presence of organic wood components the Raman spectroscopy research was performed (Fig. 4). Considering that most of the Raman bands related to the surface microstructure of carbons are present between 1000 and 2000 cm^{-1} , therefore analysis was focused on this spectra region. In all cases, the integrated areas of band D and band G are calculated from a Gaussian peak fitting function.

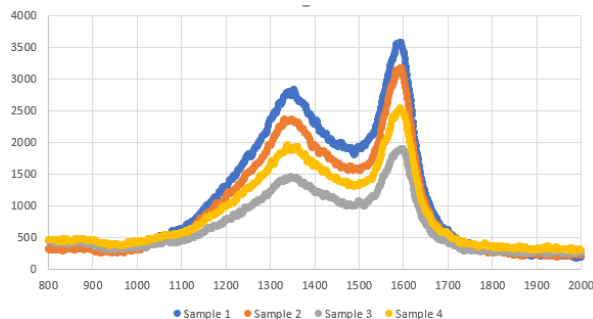


Fig. 4. Raman spectra of carbon samples

The Raman spectrum of a carbon material shows two broad peaks at about 1360 cm^{-1} and 1581 cm^{-1} , assigned to D-band and G-band, respectively. The major features of the Raman

spectra of various forms features in the spectrum of graphite. They exhibit a broad asymmetric peak centered near 1550 cm^{-1} . The intensity of the Raman peaks indicates the presence of pure carbon as a result of burnout of other organic wood components like oil, fat, resin etc. The hardness tests were performed for early wood and for late wood with a 1 kg load and dwell time of 10 s and repeated 10 times. The average hardness of the parts of early wood is significantly lower than in late wood sample, and is $10,5\text{ MPa}$ for early wood, and $24,9\text{ MPa}$ for late wood. Janka's hardness scale wood stands six classes hardness of the wood from very soft wood - 1st class to unbelievably hard wood - 6th class (Tab. 1). According to Janka's hardness scale wood samples obtained from Paulownia qualify to 1st hardness class, which is very soft wood.

Table 1. Janka's scale for determining the hardness of wood

Class	Hardness	Range MPa
I	very soft wood	under 34.3
II	soft wood	34.3-49.0
III	medium-hard wood	49.0-63.7
IV	hard wood	63.7-98.1
V	very hard wood	98.1-147.1
VI	unbelievably hard wood	above 147.1

The low hardness of Paulownia wood in comparison to other types of wood results from its porous structure, which is directly related to large annual growth of the Paulownia tree. Due to unique structures of hierarchical arrangement of hollow cells wood materials exhibits low density, high porosity with maintaining high strength and stiffness relative to their weight (Lucas, 1995).

4. Summary and conclusion

The use of natural materials in the production of composites has an advantage over the use of the other available engineering materials, i.e. it allows the use of a unique structure of living organisms, very often impossible to reproduce in "in-situ" conditions, which will ensure unrepeatability of the final material. Another unquestionable advantage of using wooden or wood-like materials is limiting the negative impact on the environment during production and processing. An example of such an application may be a fibrous structure of porous plants, especially stems and tree trunks, where after planning and performing a suitable ceramization process, such materials can be used in gas filtration systems as well as components of composites, thermal insulators, catalyst carriers or component in production of bio-oils (Singh, 2002). As a result of the research, the wood structure was determined, taking into account the porosity and pore size, mechanical properties, chemical composition of the samples after the pyrolysis process, and the effect of the carbonization temperature on the dimensions and structure of the samples. The pore size obtained after the pyrolysis process was $290.5\mu\text{m}$ and $35,8\mu\text{m}$, respectively, for spring wood and summer wood. The Raman spectroscopy research has shown that the pyrolysis temperature of 600°C is suffi-

cient to obtain samples with a pure carbon chemical composition without additions of organic components. The consistency of the chemical composition of all samples and the ease of their obtaining allow for the consideration of the obtained, as a result of pyrolysis, carbon materials as a potential reinforcement of many types of composites. Generally, mechanical properties are minimum or near minimum in the earliest annual rings, show marked improvement for a number of years, and then exhibit stability or only gradual improvement thereafter. Porous carbon materials are now expected to be used for a wide variety of industrial applications from filtration, absorption, catalysts and catalyst supports to lightweight structural components. The huge application potential of carbon precursors is confirmed by numerous publications using these materials for the preparation of composites with Al, Ti alloys and Si-based porous ceramics. Functionalised and purified biocarbon chars might be subjected to pressure infiltration with the Aluminium or Titanium alloys. Result of the infiltration of the modified and unmodified biocarbon chars are Al/C, Al/C/TiO and Al/C/TiC composite materials (Krzeminski, 2016). The synthesized carbon materials with hierarchical biomorphic structures may have a great potential for purification applications due to their large specific surface area, photocatalytic properties, and high adsorption rate (Chen, 2016). The C/TiO₂ composite sintered at high temperatures exhibited low geometrical density, thermostability, and favorable microwave absorptive properties (Qian, 2016). A wide variety of SiC-based ceramics can be fabricated by infiltration of silicon or silicon alloys into cellulose-derived carbonaceous templates, providing a low-cost route to advanced ceramic materials with near-net shape potential and amenable to rapid prototyping (Ramirez, R. 2016). It is worth to notice that the application potential of carbon materials goes beyond the field of material engineering and can be used in agriculture. Biochar has been proposed as novel material for providing soilless growth media. biochar from forest waste could be safely used as a substrate constituent and is environmentally friendly when applied due to its low salinity and low CO₂ emission (Fornes, 2018).

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基于碳材料的生物复合材料的获取

關鍵詞

碳材料
生物复合材料
木材前体
天然材料
热解
触轮。

摘要

本文的目的是介绍用于生产生物复合材料的碳预制件的特性。通过热解泡桐木材获得碳样品，复制纤维素前体的微观结构。许多表征方法如拉曼光谱，光学显微镜，硬度测试和孔径分析仪检测被用于研究产品的微结构以及碳样品的孔径。获得的结果表明，早期或晚期木模板的部分在产品的孔尺寸，比表面积和孔体积中起重要作用。这篇综述旨在全面描述炭字的发展：从木模板及其微观结构到生物形态材料的潜在应用。