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MANUFACTURING THE CELLULAR CARBON FROM PINE SAWDUST AND SUCROSE SOLUTION USING MICROWAVE HEATING

BY

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Abstract. Cellular carbon from pine sawdust and sucrose aqueous solution was experimentally manufactured. The main element of originality of the work was the realization of the carbonization process at 750°C of the pressed mixture in a strong microwave-absorbing crucible placed in the cavity of a microwave reactor. The inert atmosphere inside the crucible was obtained by periodically blowing nitrogen. Practically, the material heating was done indirectly, the thick wall of crucible being the area where the microwave power was converted into heat. Due to the high heating rate, the carbonization was achieved quickly and allowed the manufacture of cellular carbon specimens with low density and low heat conductivity. The compressive strength was acceptable, while the electrical conductivity and electromagnetic shielding effectiveness had high values.

Keywords: cellular carbon, sucrose, sawdust, microwave, carbonization.

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1. Introduction

Cellular carbon is a last-generation material extremely attractive for modern technologies involving thermal and electric energy storage, electrodes for electrochemical applications, absorbents for large molecules, electromagnetic wave absorption, catalyst support, structures for phase-change materials, ablative materials, light weight fire-resistant cores for sandwich composites, etc. (Inagaki *et al.*, 2015; Jana *et al*., 2016).

Usually, cellular carbons are manufactured by expanding pitch-based resins or organic polymer resins followed by setting and carbonization in an inert atmosphere. The cellular carbon prepared from pitch has high thermal and electrical conductivities having a homogeneous graphitic structure, while the cellular carbon made from synthetic polymer resins such as phenol-formaldehyde, polymides, polybenzoxazine, and poly(arylacetylene) is amorphous and exhibits low thermal and electrical conductivities.

Recently, a growing interest in the use of natural renewable materials (such as sucrose, lignin, olive stone, and tannin) in the manufacture of cellular carbon is exhibited in the world (Chithra *et al.*, 2020; Moussa *et al*., 2022; Tondi *et al.,* 2009). Amorphous cellular carbon with heat-insulating properties were prepared from cementing sawdust particles with sucrose (concentrations between 100-700 $g \cdot L^{-1}$) by filtration-pressing and carbonization. The density of the carbon foam was in the range of 0.15-0.35 $g \cdot cm^{-3}$, compression strength had values within the limits of 0.24-3.2 MPa, and heat conductivity was between 0.12-0.20 $W \cdot m^{-1} \cdot K^{-1}$. The cellular carbon is fireproof and has high EMI shielding effectiveness with a shielding efficiency of 25-53 dB (Chithra *et al.*, 2020). Sawdust as raw material used in this manufacturing process represents fine wood particles recovered as by-product of the wood processing industry (Wang *et al.*, 2012). According to Li *et al.*, 2015, sawdust can be liquefied and then polymerized using formaldehyde. The obtained polymer is subjected to foaming and carbonization leading to the manufacture of cellular carbon.

A new type of cellular carbon composite based on polyurethane was prepared by Udayakumar *et al.*, 2021 as an alternative solution to the conventional activated carbon derived from biomass used in catalytic application. The cellular carbon was synthesized from polyurethane foams with various graphite contents using CO_2 activation. The carbon foam composite showed better thermal stability and very low mass loss, especially below 500°C. Heat conductivity of the composite was low (0.09 $W \cdot m^{-1} \cdot K^{-1}$).

Cellular products made from cheaper raw materials (such as coal) are less expensive being used in various special applications (thermal insulation, fireproof, radar absorption, electromagnetic shielding, composite tools and composite cores, etc.). In general, commercially available cellular carbon produced from coal has the following characteristics: density in the range of 0.27-0.40 $g \cdot cm^{-3}$, heat conductivity between 0.25-25 $W \cdot m^{-1} \cdot K^{-1}$, compression strength

over 4.8 MPa, tensile strength over 1.7 MPa, electrical resistivity within the limits of 0.01-107 Ω·cm (Spradling and Guth, 2003). However, one of the main disadvantages of cellular carbon manufacturing using coal as raw material is the emission of high amounts of waste gases into the atmosphere. Several variants of precursors for cellular carbon making have been researched lately. Sucrose containing carbon, hydrogen, and oxygen concentrated in a glucose molecule and one of fructose linked together can be a suitable solution for the manufacture of this product in ecological conditions (Pellegrino, 2017).

The improvement of cellular carbon resistance was experimentally obtained using boric acid as an expanding agent (Narasimman and Prabhakaran, 2013). The H^+ ion released following the chemical reaction between sucrose and boric acid catalyzes OH^- in the condensation reaction, resulting the polymerization and expansion of melted sucrose. As a result, the carbon yield of the foam in the solid state significantly increased from 24 to 39% under the conditions of increasing the content of boric acid up to 8%. The effect of applying this technique was the improvement of the thermal insulation properties of the cellular product as follows: the density decreased to 0.11-0.16 $g \cdot cm^{-3}$, cell size increased to values between 0.67-1.17 mm, and heat conductivity decreased falling within the limits of 0.043-0.057 $W \cdot m^{-1} \cdot K^{-1}$.

The thermal foaming of activated carbon mixed with aqueous sucrose resin followed by the carbonization process was another method of cellular carbon production tested by Narasimman and Prabhakaran, 2012a. The fine active carbon powder had the role of slowing down the condensation reactions and contributed to the stabilization of the gas bubbles at the gas/liquid interface facilitating the polymer resin expansion. The carbon resulting from the carbonization process has bound the activated carbon particles. The final product had the density in the range of 0.138-0.22 $g \cdot cm^{-3}$, the cell size varying between 0.02-3 mm. Compression strength had values within wide limits (0.42-3.4 MPa). Another method of producing cellular carbon used aluminum nitrate (between 0.5-4 wt. %) as an expanding agent in melted sucrose (Narasimman and Prabhakaran, 2012b). The specific operations of this method were: mixing, heating/expanding at 150°C in an open mold, dehydration at 250°C, and carbonization in a neutral atmosphere at 900°C. The cellular carbon specimens had very low density within the limits of 0.053-0.083 $g \cdot cm^{-3}$, and cell size between 0.83-1.55 mm.

Authors of the current paper previously tested the manufacture of cellular carbon using wood biomass in the form of sawdust and sucrose solution (Păunescu *et al*., 2022). Carbonization of the mixture was performed through unconventional microwave heating at 750°C, the pressed material being introduced into a silicon carbide (SiC) crucible thermally protected on the outside with ceramic fiber mattresses. The optimal cellular carbon specimen had low density (0.28 $g \cdot cm^{-3}$), low heat conductivity (0.11 $W \cdot m^{-1} \cdot K^{-1}$), relatively high compression strength (3.5 MPa), high electrical conductivity (29.8 $S \cdot m^{-1}$), and

very high shielding effectiveness (46 dB). Very low specific energy consumption (0.785 $kWh \cdot kg^{-1}$) was recorded.

The work presented below aimed at the manufacture of cellular carbon in slightly modified technological conditions compared to the experiment mentioned above. The 0.8 kW-experimental microwave equipment used for the carbonization process was replaced by choosing a microwave reactor with a higher installed power (3 kW) and the SiC-microwave susceptible crucible had a much larger wall thickness (20 mm) allowing only the indirect heating of material with lower heating rates. The used materials were also wood sawdust and sucrose solution, but a type of wood (pine) more readily available as a by-product of the wood processing industry was chosen. In terms of quality, the aim was obtaining lower density, as well as significantly lower heat conductivity and maintaining the high level of electrical conductivity and electromagnetic shielding effectiveness.

2. Materials and Methods

Two environmentally friendly materials (wood in the form of sawdust recovered from processing workshops and sucrose from sugar cane and sugar beet crops) make up the starting mixture for the manufacture of cellular carbon. Under the current global conditions in which environmental protection is one of humanity's major concerns, the use of natural materials or those that represent an industrial by-product for manufacturing a new product of great interest without affecting the quality of the environment is remarkable.

Sucrose ($C_{12}H_{22}O_{11}$) comes from plant sources. Two main types of crops that contain important amounts of sugar (12-20% of the dry weight of plants) are sugar cane and sugar beet. Natural sucrose was commercially procured in the state of crystalline powder soluble in distilled water.

The sawdust-supplier wood used in this experiment was pine from the softwood group intensively utilized in construction and furniture design. Processing the sawdust for the use in this experiment has meant its grinding in a ball mill to the particle size below 170 μm. Then, the sawdust powder was dissolved in the aqueous solution of sucrose by stirring resulting a slurry. This was pressed in a cylindrical mold and dried in the oxidizing atmosphere of laboratory electric oven. The next stage of the process was carbonization of the pressed material into a SiC-cylindrical crucible at 750°C. The material was freely deposited on a 3 mm-metal plate placed at the base of crucible. The upper opening of the crucible was covered with a SiC-lid provided with 20 mm-axial hole. The role of this hole was both to facilitate the visualization of the hot material surface with the pyrometer and to periodically blow nitrogen inside the crucible, avoiding the formation of an oxidizing atmosphere capable of igniting the wood-based mixture. The crucible was protected on the outside with thick mattresses (25 mm) made of ceramic fiber heat-resistant up to 1200°C and forcibly mounted into the

reactor cavity. Measuring the temperature radiated by the upper surface of the heated sample was made with the radiation pyrometer fixed above the reactor (Fig. 1).


a


b

Fig. 1 – Experimental microwave equipment
a – SiC-crucible; b – 3 kW-microwave reactor.

Recently, the literature highlighted the slight tendency exhibited towards the application of unconventional microwave heating in some biomass pyrolysis and carbonization processes (Nizamudin *et al*., 2018). The mentioned work has found the energy efficiency of this procedure compared to conventional heating techniques.

Four experimental versions of cellular carbon specimens were prepared using sucrose and pine sawdust. Sucrose (in crystalline state) was dissolved in distilled water in four concentrations corresponding to each experimental version: 690, 730, 770, and 810 $g \cdot L^{-1}$. The dry sucrose amount varied within the limits of 192-207 g and the total dry mixture amount was adopted at the constant value of 345 g. Under these conditions, the dry sawdust amount had decreasing values in the four versions from 153 to 138 g. Distilled water quantity decreased from 278 to 256 g taking into account adopted values of sucrose concentration mentioned above. The composition of experimental versions is shown in Table 1.

Table 1
Composition of experimental versions

Composition	Version 1	Version 2	Version 3	Version 4
Dry sucrose				
- amount (g)	192	197	202	207
- weight ratio (wt. %)	55.7	57.1	58.6	60.0
Dry pine sawdust				
- amount (g)	153	148	143	138
- weight ratio (wt. %)	44.3	42.9	41.4	40.0
Total dry mixture (g)	345	345	345	345
Distilled water (g)	278	270	262	256

The following methods for characterization carbon foam specimens were used. Density was determined based on the gravimetric method (Metrology, 2015). Heat conductivity (at 30°C) was measured with HFM 446 Lambda apparatus using the heat-flow method (SR EN 1946-3: 2004). Compression strength was identified with 100 kN-hydraulic axial press machine (EN 826: 2013). The microstructural peculiarities of samples were examined with Biological Microscope MT5000 model with captured images 1000 x magnification. Electrical conductivity could be measured using the method presented in (Grivei and Probst, 2003) utilizing an original laboratory equipment and the electromagnetic shielding characteristics of specimens were determined using the method of nested reverberation chamber in the frequency band 1-4 GHz (Moglie *et al*., 2012).

3. Results and discussion

In general, the carbonization stage of carbon-containing materials is of particular importance for obtaining the microporous structure of cellular carbon. It was found that the use of a carbonization temperature of wood in the absence of air between 400-1100°C increases the pore size and the yield of carbon compared to carbonization processes at low temperature (Li *et al*., 2008). The optimal carbonization temperature was experimentally determined by authors of the current paper in a previous similar work (Păunescu *et al*., 2022) at a value around 750°C.

Considering that the dry amount of the starting material mixture was constant at the value of 345 g, the cellular products corresponding to the four experimental versions were weighed to identify the mass loss of each specimen. In terms of energy, the specific energy consumption value characteristic for the experimental versions was determined. The duration of the microwave heating process was timed and the value of energy consumption was counted. The results are presented in Table 2.

Table 2
Characteristics of the carbonization process

Characteristic	Version 1	Version 2	Version 3	Version 4
Dry mixture amount (g)	345	345	345	345
Cellular carbon amount (g)	310.5	315.7	320.8	327.7
Weight loss (%)	10.0	8.5	7.0	5.0
Carbonization temperature (°C)	750	750	750	750
Heating time (min)	30	30	30	30
Specific energy consumption (kWh/kg)	1.01	0.99	0.97	0.95

According to the data in Table 2, the mass loss following the carbonization process as a stage of cellular carbon manufacturing is different and is influenced by the sucrose concentration in the starting mixture. The mass loss decreased from 10% (in version 1) to 5% (in version 4) corresponding to concentrations within the limits of 690-810 $g \cdot L^{-1}$. Carbonization through the microwave heating procedure proved efficient in terms of energy, the duration of the process being short (30 min) and the specific energy consumption having low values (between 0.95-1.01 $kWh \cdot kg^{-1}$).

The physical appearance of the four cellular carbon specimens manufactured by the technique described above is shown in Fig. 2.

Fig. 2 – Physical appearance of cellular carbon specimens
a – version 1; b – version 2; c – version 3; d – version 4.

Results of the investigation of cellular carbon specimen characteristics made in this experiment are shown in Table 3.

Table 3

Characteristics of cellular carbon specimens

Characteristic	Version 1	Version 2	Version 3	Version 4
Density ($g \cdot cm^{-3}$)	0.22	0.20	0.17	0.15
Heat conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	0.082	0.074	0.065	0.060
Compression strength (MPa)	3.1	2.9	2.6	2.3
Electrical conductivity ($S \cdot m^{-1}$)	29.6	27.8	26.4	24.8
Electromagnetic shielding effectiveness (dB)	46	42	38	32
Cell size (μm)	110-230	190-250	210-310	240-490

The microstructural aspect of the four cellular carbon specimens is presented in Fig. 3.

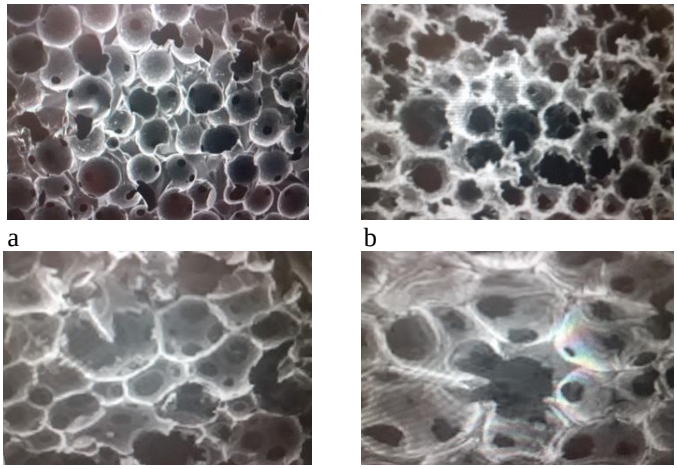

Fig. 3 – Microstructural aspect of cellular carbon specimens
a – version 1; b – version 2; c – version 3; d – version 4.

Examining the data in Table 3 shows the achievement of the main objectives of the work. Thus, the value level of density and heat conductivity of cellular carbon specimens was lowered to 0.15-0.22 $g \cdot cm^{-3}$ and 0.060-0.082 $W \cdot m^{-1} \cdot K^{-1}$, respectively, below the level obtained by the authors' team in the previous similar work (Păunescu *et al*., 2022). Also, the cell size of the sample

microstructures was very low, being between 110-230 μm (version 1) and between 240-490 μm (version 4). Authors explained this improvement in thermal insulation properties by adopting the indirect microwave heating system, which reduced the average heating rate during the carbonization process, bringing it closer to typical values of conventional heating.

According to the literature, in general, cellular carbon specimens characterized by thermal insulation properties (low density and low heat conductivity) exhibit the tendency to develop a semi-open microstructure, in which the cells communicate with each other through the neighboring walls. However, the thickness of cell walls and the existence of struts in the intercellular spaces have the ability to constitute a network that maintains the mechanical strength of the cellular product at an acceptable level. In the experiment described in this paper, the appearance of interconnected cells is more prominent in versions where the sucrose concentration is higher. Also, the cell size is increasing and the compression strength is slightly decreasing.

The electrical conductivity as well as the electromagnetic shielding effectiveness were maintained at high values (up to 29.6 $S \cdot m^{-1}$ and 46 dB, respectively) with a tendency to decrease with the increase in sucrose concentration in the initial mixture.

4. Conclusions

The work aimed at manufacturing cellular carbon using as raw material pine sawdust recovered from a wood processing workshop and an aqueous solution of sucrose as a natural material. According to a known technique, the sawdust was mixed with the sucrose solution resulting a paste. The mixture in form of the paste was pressed and dried into a mold and then removed and freely deposited into high microwave-absorbing crucible introduced in the microwave reactor. The non-oxidizing atmosphere inside the crucible required to avoid ignition/burning the carbonic mixture was achieved by periodically blowing nitrogen through the lid hole. The carbonization process as a stage of cellular carbon manufacturing was the main element of work originality. By adopting a crucible with thick wall (20 mm), the indirect microwave heating was chosen creating conditions for reducing the density (between 0.15-0.22 $g \cdot cm^{-3}$) and the heat conductivity (in the range of 0.060-0.083 $W \cdot m^{-1} \cdot K^{-1}$) as well as for obtaining very fine porosity under 500 μm). The compressive strength kept acceptable values (2.3-3.1 MPa). Similarly, the electrical conductivity had high values (within the limits of 24.8-29.6 $S \cdot m^{-1}$) and the electromagnetic shielding effectiveness was excellent (between 32-46 dB).

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FABRICAREA CARBONULUI CELULAR DIN RUMEGUȘ DE PIN ȘI SOLUȚIE DE ZAHAROZĂ UTILIZÂND ÎNCĂLZIREA CU MICROUNDE

(Rezumat)

Carbonul celular din rumeguș de pin și soluție apoasă de zaharoză a fost fabricat experimental. Principalul element de originalitate al lucrării a fost realizarea procesului de carbonizare a amestecului presat la 750°C într-un creuzet puternic absorbant de microunde plasat în cavitatea unui reactor cu microunde. Atmosfera inertă din interiorul creuzetului a fost obținută prin suflarea periodică a azotului. Practic, încălzirea materialului s-a făcut indirect, peretele gros al creuzetului fiind zona în care puterea microundelor a fost convertită în căldură. Datorită vitezei mari de încălzire, carbonizarea a fost realizată rapid și a permis fabricarea de produse de carbon celular cu densitate scăzută și conductivitate termică scăzută. Rezistența la compresiune a fost acceptabilă, în timp ce conductivitatea electrică și eficacitatea ecranării electromagnetice au avut valori ridicate.