Fabrication of low density carbon foams by gel-casting method from sucrose/microcapsules

H. H. Yu[a], H. Liu[a], H. K. Chen[b], S. M. Wang[a], Q. Z. Liu, X. Li[a,*]
[a]School of Material Science and Engineering, Shenyang Ligong University, Shenyang 110159, China
[b]Science and Technology on Advanced Functional Composites Laboratory,Aerospase Research Institute of Material and Processing Technology100076 China

The carbon forms made from sucrose and microcapsules have successfully fabricated using gel-casting method. The structure, density, compressive strength and thermal conductivity were characterized. Carbon foams have porous structure of open cells and closed cells. The density of carbon foams is regulated in the range of 0.29 – 0.65 g/cm3, whereas the compressive strength is in the range of 1.03 – 20.25 MPa. The thermal conductivity at room temperature of carbon foams can be as low as 0.11 W/m·K . Therefore, these carbon foams have potential for use as the thermal insulator.

1. Introduction

Due to its special pore structure, carbon foams have many excellent properties such as low density, good electronic conductivity, thermal shock resistance, adjustable thermal properties[1]. Hence, carbon foams are attractive candidates for high temperature thermal insulation, electrodes, light weight structural components, industrial adsorption, and so on[2-6].

In the last decades, researchers focused on finding new carbonaceous precursors (such as coal, mesophase pitch and, polyimide, etc.) for the preparation of carbon foams[7-9]. Nowadays, the utilization of renewable organic molecule (such as tannin, sucrose and lignin) for the synthesis of carbon foams has received great attention due to the depletion of fossil energy[10-14]. Due to its high carbon content, water-solubility sucrose has been identified as one of the most suitable carbonaceous precursors. The team of P. Jana[15] synthesize sucrose-based carbon foams with ultralow density (0.04–0.075 g/cm^3) and ultralow thermally insulating (0.042-0.065 W m^{-1} K^{-1}). However, these carbon foams have a low carbon yield, resulting in low compressive strength (0.11-0.23 MPa). Researchers have attempted to improve the mechanical properties of sucrose-based foams carbons by adding aluminum nitrate[12], kaolin or boric acid [13]. Although the mechanical properties of the samples obtained by these methods are improved, they are still lower than the mechanical properties of tannin-based carbon foam (12 MPa).

The team of Y. Yao [14]fabricates carbon foams with high mechanical (3.0 – 108.0 MPa) and ultralow density (0.17 – 0.93 g/cm^3) by combined physical foaming and gel-casting techniques. Preparation of foams carbon by gel-casting technique, after the dehydration and thermal polymerization, the firm sucrose/polyacrylamide hydrogel matrix is polymerized into a high cross-linking degree and reacted without destroying the three-dimensional polymer network, resulting in higher carbon yield and less cracks, which increases the strength of carbon foams. If we immobilized uniform hollow spheres into the three-dimensional polymer network, an interesting product with large porosity would be obtained. Herein, uniform hollow spheres are introduced by using microcapsules.

In this study, we reported for the preparation of sucrose-based carbon foams with high mechanical properties by using gelcasting technique. By adding microcapsules as porous template,

---

* Corresponding author: lx80ws@126.com

carbon foams with uniform cell structure can be obtained. To our knowledge, this is the first example to show that carbon foams is prepared using microcapsules as porous template and sucrose as carbon precursor by gel-casting technique.

2. Experimental

Sucrose, N,N,N′,N′-tetramethyl ethylenediamine(TEMED) N,N′-methylene bisacrylamide (NMBA), Acrylamide (AM), and ammonium persulfate (APS) were obtained from Siopharm Chemical Reagent company. Microcapsules were obtained from Matsumoto Yushi-Seiyaku Co., Ltd.

The monomer solution was prepared by mixing AM and NMBA of which the ratio is 9:1 in 40 ml deionized water. In the meanwhile, the sucrose were dissolved in monomer solution to form a pre-solution. Then, different contents of microcapsules were added into the solution with high-speed. After that, the initiator (APS) and catalyst (TEMED) were added slowly into the solution with low-speed continuous stirring. This solution was casted into molds to prepare precursor by the initial gelation.

The precursor were dried in the draught drying cabinet at 40 °C for 48 h. Then, all samples were thermal polymerized in air atmosphere at 200 °C for 5 h. After that, these samples were carbonized in the inert atmosphere at 1000 °C for 2 h. Ultra-high purity argon gas (99.999%) maintaining all heat treatment of foams was used as the inert atmosphere. The heating rate used for all heat treatment was 2 °C/min.

The thermo-decomposition of the precursor was carried out in argon atmosphere using a thermo-gravimetric analyzer (NETZSCH, STA449F3). The XRD patterns were obtained in an X-raydiffraction (RigakuUltima IV) using CuKα radiations(λ = 0.15406 nm).The microstructure carbon foams was observedby scanning electron microscopy (SEM) (Japan Electronics, JEOL6105A) at an accelerating voltage of 15 kV. The compressive strength of the carbon foams was measured using a universal testing machine (Instron5050) at acrosshead speed of 0.5 mm/min with 25mm×25mm×12mm samples (ASTMstandardC365/C365M-05). Thermal conductivity measurements were carried out at roomtemperature by the heat flow method (NETZSCH, HFM446).

3. Results and discussion

3.1.Foam carbon precursor carbonization process

Fig.1 shows the TG curves in argon atmosphere of carbon foams precursors prepared with 120 ml microcapsule. It is observed clearly from Fig.1 that the weight loss is about 25% in the temperature range of 20 -200 °C. The weight loss in this temperature range is mainly due to dehydration[14]. Weight loss observed in the temperature range of 200 - 600 °C is about 38%. It suggests that the loss of carbon as CO and CO_2 takes place due to the cleavage of-C-O-C- and O-C=O groups along with the dehydrationin argon atmosphere[13]. When the temperature is above 600 °C, the weight loss curve changes gently, and the pyrolysis rate slows down.
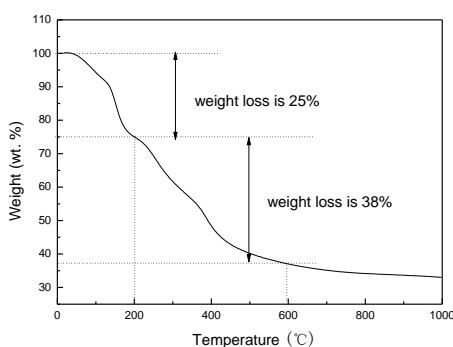

Fig.1. The TG curves of carbon foams precursors in argon atmosphere.

Fig.2 shows the XRD spectra of the precursor and carbonized carbon foams at 1000 °C. Fig.2(a) shows that largely disordered state is indicated by the broad and low-intensity diffraction peaks for the samples. After carbonization, there is still the broad and low-intensity diffraction peaks, but the diffraction peaks have appeared on the (001) and (002) planes. The result shows that carbon foams have not been formed with graphite structure but close to the mesopitch-derived graphitic mesoporous carbon [16].
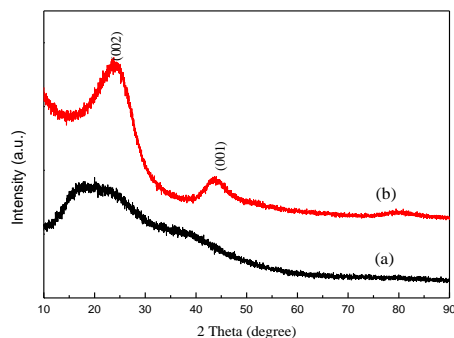

Fig. 2. The XRD spectra of the precursor and carbon foams:
(a) the precursor, (b) carbonized carbon foams at 1000 ℃.

3.2. The microstructure of carbon foams

Fig. 3 shows the SEM micrographs of the carbon foams with different microcapsule contents. The carbon foams have an interconnected cellular structure with spherical cells which are formed by microcapsules in the precursor. The spherical cells are interconnected by intact junctions and cell walls, and have both open and closed pore structures. With the increase of microcapsule content, the number of pores increased, and the cell structure gradually became complete and evenly distributed. The pore walls between the pores become thinner, and the porosity increases. The formation of the open cells structure can be explained as follows: the microcapsule were ruptured due to the exothermic reaction during the polymerization of gel-casting; in the meanwhile, this pore structure was retained in the sucrose/polyacrylamide hydrogel organic foams.
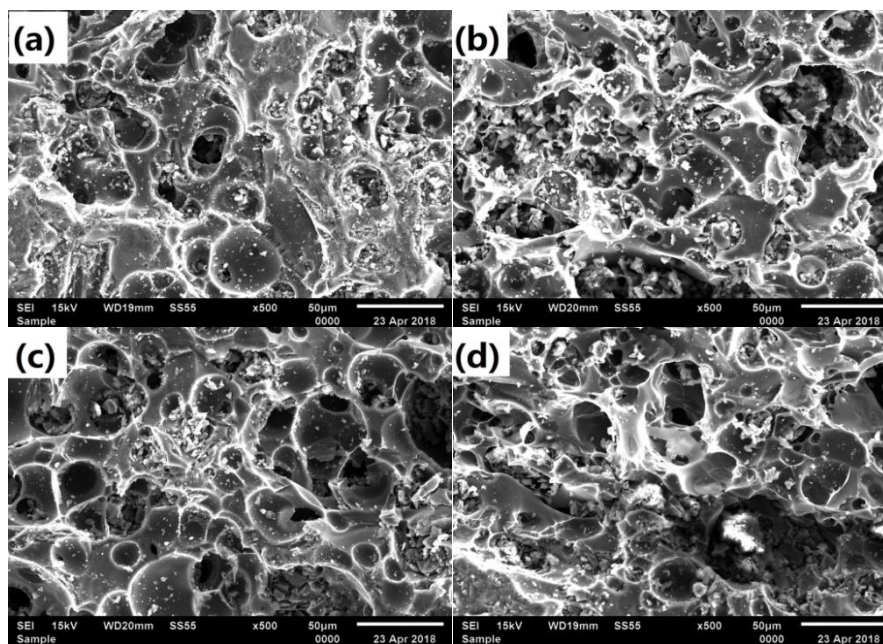

Fig. 3. The SEM graphs of the carbon foams with different microcapsules contents
(a) 40ml (b) 80ml (c) 120ml (d) 160ml.

3.3.The Compressive strength andDensities

The compressive strength and densities of carbonfoams with different microcapsules content are shown in Fig.4. With increasing the content of microcapsules from 40 ml to 160 ml, the density of carbon foams decreased as well, and reached the minimum of 0.29 g/cm^3 at 160ml of microcapsules content. By adjusting the contents of microcapsules, the densities of carbon foams vary widely from 0.29 g/cm^3 to 0.65 g/cm^3. The change of compressive strength had the similar trend as the change of density, compressive strength of carbon foams is controlled in a wide range from 1.03 MPato 20.25 MPa.
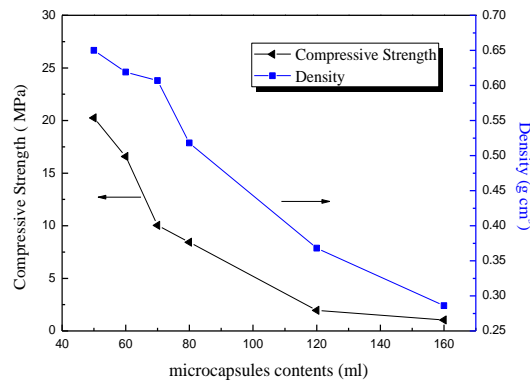

Fig. 4. The compressive strength and densities of carbon foams prepared at various microcapsules contents.

The changes of compressive strength with density (d) can be described by the following equation[18]:
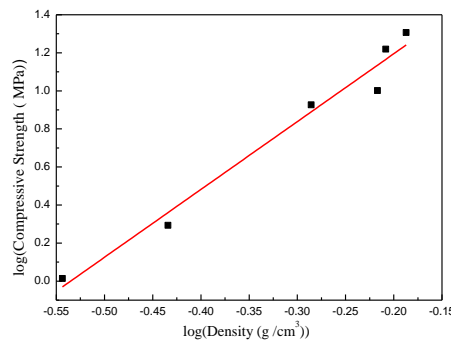
$$\sigma \propto \sigma_s d^{\alpha} \quad (1)$$

Fig.5. Log of density versus log of compressive strength plot of carbon foams prepared at different microcapsules contents.

In the equation, σ_s represents the compressive strength value of the (non-porous)materials, and the index α depends on the cellular materials deformation mechanics and structure.

The fitted straight lineis obtained according to Eq. (1) as shown in Fig.5. It has been reported to use Eq. (1) to similar fit carbon foams by literature. It is claimed that the reason for the poor fitting is cell sizes, nature of struts and microcracks of carbon foams. In our work, the exponent values of α for prepared carbon foams is 1.91. The theoretical values of α of open-cell and closed-cell structure are 1.5 and 2, respectively [19]. The exponent values of 1.91 of between 1.5 and 2 suggest that the pores are not all closed-cell structures, which can also be demonstrated from the pores structure in Fig. 3.

3.4The thermal conductivity of carbon forms

Dou to the closed-cell and amorphous structure, the non-graphitized carbon foams have lower thermal conductivity than graphitized carbon foams. For non-graphitized carbon foams, the thermal conductivity factors are affected by the density, strut nature, cell size, and cell wall thickness.

The Fig. 6 shows that the density plotted as a function of the thermal conductivity at room temperature of the carbon foams prepared at different microcapsules contents. As shown in fig. 6, the thermal conductivity of carbon foams increased from 0.082 to 0.11 W/m·K when the density increased from 0.29 to 0.65 g/cm^3.The minimum value of thermal conductivity(0.082 W/m·K) is slightly higher that reported for carbon foams (0.057 W/m·K)[20] and (0.09 W/m·K) [21]. However, the density of the carbon foams (0.29 g/cm^3) is also higher than that reported for carbon foams (0.016 g/cm^3) and (0.018 g/cm^3). Highly porous materials having constant pore structure but different total porosity shows a linear increase in thermal conductivity with the density in a small range of porosities.

In the range of small porosities, the thermal conductivity increases linearly with density, when the porous material has a constant pore structure, but the total porosity is different. As shown in Fig. 6, the thermal conductivity and density plot deviates greatly from linearity. In the present case, the graph largely deviates from linearity. This is attributed to the presence of microcracks in the cell walls of carbon foams prepared at different microcapsules contents.
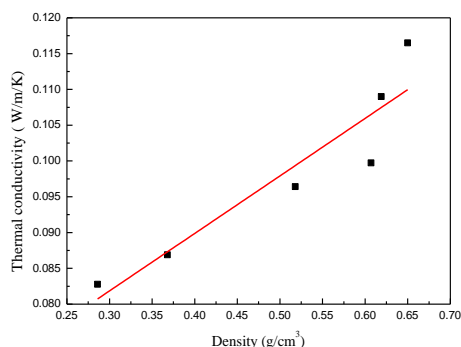

Fig.6. The thermal conductivity at room temperature of carbon foams with different density.

4. Conclusions

With microcapsules as porous template, carbon foams are prepared by using gelcasting technique from sucrose/polyacrylamide hydrogel. By the thermal polymerization and carbonization, a high cross-linking degree of sucrose/polyacrylamide hydrogel is formed, resulting in the high carbon yield and non graphite structure .Carbon foams prepared by this method are provided with interconnected cellular structure with spherical cells. The cell structure is controlled by the contents of microcapsules, leading to the regulated density (0.29 – 0.65 g/cm^3) of carbon foams. As a result of the control of cell structures, compressive strength of carbon foams is in thewide range of 1.03 MPa to 20.25 MPa. In addition, the thermal conductivity of carbon foams increased from0.082 to 0.11 W/m·K.

Acknowledgments

974

References

[1] M. Inagaki, J. Qiu, Q .Guo, Carbon **87**,128(2015).
[2] J. Y. Qu, Q. Han, F. Gao, J. S. Qiu, New Carbon Materials **32**, 86(2017).
[3] S. Wang, N. Xiao, Y. Zhou, Z. Ling, M. Li, J. Qiu, Carbon **105**, 224(2016).
[4] N. Amini, K. F. Agueyzinsou, Z. X. Guo, Carbon **49**, 3857(2011).
[5] N. C. Gallego, J. W. Klett. Carbon **41**, 1461(2003).
[6] E Rodriguez, R Garcia, Fuel Process. Technol. **156**, 235(2017).
[7] S. Li, Y. Tian, Y. Zhong, Y Xi, S. Yan, Q. Guo, J. Shi, L. Lang, Carbon **49**, 618(2011).
[8] G. Tzvetkov, B. Tsyntsarski, K. Balashev, T. Spassov, Micron **89**, 34(2016).
[9] J. Seo, H. Park, K. Shin,S. H. Baeck, Y. Rhym, E. S. Sang, Carbon **76**, 357(2014).
[10] J. Y. Qu, Q. Han, F. Gao, J. S. Qiu, New Carbon Materials **32**, 86(2017).
[11] G. Tondi, V. Fierro, A Pizzi, A. Celzard, Carbon **47**, 1480(2009).
[12] R. Narasimman, K. Prabhakaran, Carbon **50**,1999(2012).
[13] R. Narasimman, K. Prabhakaran, Carbo **55**, 305(2013).
[14] Y. Yao, F. Chen, X. Chen, Q. Shen, L. Zhang, Diam. Relat. Mater. **64**,153(2016).
[15] P. Jana, V. Fierro, A. Celzard, Carbon **62**, 517(2013).
[16] K. Prabhakaran, P. K. Singh, N. M. Gokhale, SC Sharma, J. Mate. Sci. **42**(11), 3894(2007).
[17] L.J. Gibson, M.F. Ashby, Cellular Solids: Structure and Properties, Cambridgeuniversity press, Cambridge Solid State Press, 62 (1997).
[18] W. S. Sanders, L. J. Gibson, Mater. Sci. Eng. A **347**(1), 70(2003).
[19] R.Narasimman, K.Prabhakaran, Carbon**55**, 305(2013).
[20] X. Li, M. C. Basso, F. L. Braghiroli, V. Fierro, A. Pizzi, A. Celzard, Carbon **50**, 2026(2012).