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Cellular carbon microstructures developed by using stereolithography

Xu Chen, Guangbin Zhao, Yanlong Wu, Yajiang Huang, Yaxiong Liu*, Jiankang He, Ling Wang, Qin Lian, Dichen Li

State Key Laboratory for Manufacturing System Engineering, School of Mechanical Engineering, Xi'an Jiaotong University, 710054, Xi'an, ShaanXi, China

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ABSTRACT

Additive manufacturing has attracted much attention to generate structures containing ordered cells and customized shapes with various materials. A simple method was proposed to develop net-shape cellular carbon microstructures (CCMs) with controllable low shrinkage by using stereolithography. The polymer architectures, made of photosensitive resins, and sodium chloride were directly used as carbon precursors and granular support during carbonization, respectively. In addition, graphite powder was introduced into the granular support, which significantly enhances the mechanical property and electrical conductivity of the CCMs, and low graphite content has no significant effect on the volume shrinkage. The extremely high-porosity CCMs without distortion and breakage were obtained, showing controllable low volume shrinkage (44%–52%) with extremely low carbon yield (6%). The microstructure, mechanical property and electrical conductivity were measured and compared. It was found that the CCMs with graphite particles attaching on their surfaces show smooth surfaces with fewer defects, and possess great mechanical property (compressive stress and elastic modulus are 0.36 Mpa and 23.9 Mpa, respectively) and electrical conductivity (0.43 S/cm), which makes them promising materials for many potential applications.

1. Introduction

Porous carbon structures, noted as carbon foams, have found many applications including catalyst materials for chemical reactions [1], containers for thermal energy storage [2–4], electrode materials for batteries [5,6], materials for electromagnetic shielding [7], absorbers for organic solvents [8,9]. This is attributed to the distinctive and excellent properties of carbon foams, e.g. light weight, high interconnected porosity, good thermal and electrical conductivity and hydrophobic property.

In most cases, carbon foams can be classified into graphitic and glassy types based on graphitization degree. As reported in the literature [10], the preparation processes of carbon foams, despite graphitic or glassy, mainly include foaming with carbonization, template carbonization and others. Many graphitic carbon foams were produced by applying foaming method on coal, coal tar pitch and petroleum pitch, which have good mechanical property, good thermal and electrical conductivities, but low porosity and uncontrollable random cells [11–13]. There is an increasing interest in preparing highly porous carbon foams with random cells by polyurethane (PU)-template method with various precursors (e.g. phenol or resorcinol-formaldehyde resin [3,14–16], furfural resin [17], polyimide [18] and pitch-based materials [19,20]). Furthermore, several researchers reported simple methods to fabricate carbon foams by direct carbonization of melamine foams which have extremely low density and high porosity [8,9]. However, high shrinkage and deformation appear due to the low carbon yield of melamine (~9%). All these random carbon foams result in some beneficial properties, however, some disadvantages may occur, like uncontrollable macro shapes, random cell structure, even high shrinkage and deformation.

It has been shown that the material utilization and properties can be dramatically improved by introducing ordered cells [21,22] which can be easily fabricated by using additive manufacturing. However, only a limited number of investigations regard to the preparation of carbon cellular structures by using additive-manufactured polymer structures in recent years. This is due to the fact that the polymers applied to additive manufacturing are mostly thermoplastic, or have a considerable weight loss during carbonization, like the photosensitive resins [23]. A. Szczurek et al. [24] attempted to develop carbon periodic cellular structures under hydrothermal conditions by using 3D-printed polymer

* Corresponding author.
E-mail address: yaxiongliu@163.com (Y. Liu).

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architectures as templates, which presented higher elastic modulus than random carbon foams, but a high volume shrinkage over 72.3%. J. Bauer et al. [25] created ultra-strong glassy carbon nanolattices with a volume shrinkage of 80% by direct pyrolysis of polymer microlattices fabricated by 3D direct laser writing. These carbon structures exhibit ordered cells and excellent mechanical property, but the extremely high volume shrinkage remains unsolved. In most cases, the distortion of porous carbon structures will be greater when the volume shrinkage is larger, due to the accumulation of anisotropic effects of gravity and friction during carbonization. To our best knowledge, no net-shape ordered carbon structure with low shrinkage has been prepared by using additive manufacturing so far.

The present paper proposes a simple mothed to develop net-shape cellular carbon microstructures (CCMs) with controllable low volume shrinkage by using the polymer architectures from stereolithography as carbon precursors. The porous polymer architectures were carbonized without any chemical pre-process, but with sodium chloride (NaCl) as granular support during carbonization. In addition, graphite powder was introduced into the granular support to enhance the mechanical property and electrical conductivity of the CCMs. To our best knowledge, no similar process by using granular support material has been reported so far. The granular support can prevent porous polymer architectures from shrinking and deforming freely, and hence decrease the anisotropic effects of gravity and friction. Remarkably resulting in controllable low volume shrinkage, this method can be adopted to produce porous net-shape carbon structures from thermoset polymers, even those having low carbon yield.

2. Materials and methods

2.1. Preparation of the CCMs

Rhombic dodecahedron was employed as the unit cell of the polymer architectures in consideration of that PU-template carbon foams are typically composed of dodecahedron/polyhedron cells [3]. Fig. 1a shows the unit cell with design and calculation parameters, generated by a 3D computer-aided design software (Autodesk Inventor 2012, AutoDesk, USA). The strut thickness and pore size were defined as d and D, respectively; and the strut length and cell size were defined as l and L, respectively. Then, the unit cell was saved as STL format and transferred into Magics 19.01 (Materialise, Belgium), a STL editor software, to obtain a numerical model with a $4 \times 4 \times 4$ array of the unit cells. The strut thickness has a more remarkable influence on the properties of the resulting CCMs than other parameters in this experiment. Thus, we chose two polymer architectures (#1 and #2) with different strut thickness ($d = 0.3$ and 0.4 mm) and constant pore size ($D = 0.6$ mm) as carbon precursors (see Table 1), and the corresponding CCMs were called CCM#1 and CCM#2, respectively.

The polymer architecture (see Fig. 1b) was fabricated by stereolithography with a 3D printer (SPS600, XJRP, China). This 3D printer has the maximum resolutions of 0.05 mm and 0.08 mm for planar and vertical directions, respectively. The photosensitive resins (SPR6000, Zhbond Technology, China) containing acrylics and epoxies were used in the stereolithography process. A thermoset polymer with three-dimensional crosslinking structure and high molecular weight can be produced when strong covalent bonds form among the polymer precursors (acrylics and epoxies) during stereolithography. Generating supports is unneeded in the process of building small cellular structure with suspending struts in stereolithography because the photosensitive resins can act as supports.

Fig. 2 shows the flowchart of the process used for developing the CCMs. The design and stereolithography of the polymer architectures have been described above, respectively. Then, pure NaCl powder was ball milled and sieved to a size of 100–200 μm (see Fig. 3). The powder with suitable size distribution can result in good flowability [26], facilitating the penetration of particles into the pores of the porous polymer architectures. In addition, graphite powder (JIE CHENG GRAPHITE, China) was introduced into the granular support (at 0 wt%, 1 wt%, 2 wt%, 3 wt% and 4 wt% graphite content) to enhance the mechanical property and electrical conductivity of the CCMs. Meanwhile, the flowability of the granular support mixed with graphite powder can be improved [27]. Subsequently, the obtained granular support with different graphite contents was dried at 150 °C for 2 h in a vacuum oven.

Table 1
Design and calculation parameters of the unit cells (see Fig. 1(a)) in this experiment.

Cell parameters	#1	#2
d (mm)	0.3	0.4
D (mm)	0.6	0.6
l (mm)	0.955	1.061
L (mm)	2.205	2.450

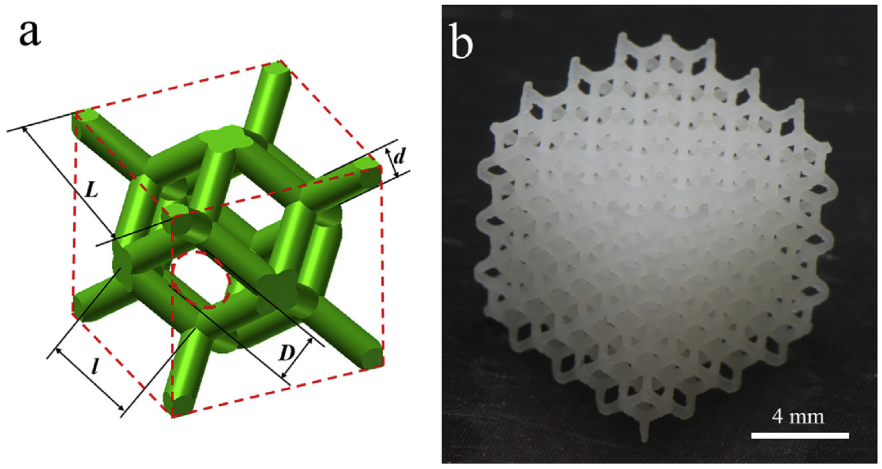

Fig. 1. (a) Unit cell with parameters: strut thickness d, pore size D, strut length l and cell size L; (b) polymer architecture #1 by Stereolithography. (A colour version of this figure can be viewed online.)