RSC Advances

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

RSC Advances

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Synthesis of carbon/carbon composites by hydrothermal carbonization using starch as carbon source

Ouyang Haibo[a*], Li Cuiyan[a], Huang JianFeng[a], Fei Jie[a]

[a] College of Materials Science and Technology, Shaanxi University of Science and Technology, Xi'an, Shaanxi, 710021, China

Abstract: Carbon/carbon (C/C) composites were fabricated by hydrothermal carbonization (HTC) using starch as carbon source. The C/C composites were densified by 10 cycles of HTC treatment, each consisting of 2 hours. The density of the composites can achieve 1.23 g/cm^3 and the porosity is about 10.9%. The matrix of the C/C composites is an amorphous carbon functionalized with hydroxyl and carboxyl groups. The flexural strength and modulus of the composites can reach 146 MPa and 9.6 GPa. The fracture of the composites presents a typical pseudo-plastic fracture characterization. These results suggest that the new C/C composites can be used as engineering materials and biomedical materials. HTC technique is an efficient and environmental-friendly route to fabricate C/C composites.

Key words: Carbon materials; Composites materials; Hydrothermal carbonization; Microstructure; Flexural strength.

1. Introduction

Carbon/carbon (C/C) composite is considered as a family of advanced composite materials, due to its superior mechanical properties at high temperatures, resistant to thermal expansion, excellent wear resistance, and good biocompatibility [1]. The unique

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[*] Corresponding author. Tel./fax: +86 029 86168803.

E-mail addresses: ouyangsust@126.com (Ouyang H.B.)

features make this material abundantly available for industrial applications. C/C composites can be manufactured by different techniques, such as pyrolysis of thermosetting resins, pyrolysis of pitch, and chemical vapor infiltration (CVI) route using hydrocarbon gases [1, 2]. The carbon sources used for the fabrication of C/C composites are fossil fuels and their derivatives. The pyrolysis of these fossil fuels and their derivatives need a high temperature around 1000 ^{o}C. However, fossil fuels are subject to depletion, pollution, and environmental hazards as they are consumed.

Recently, synthesis of carbonaceous materials by hydrothermal carbonization (HTC) has become an emerging method from the viewpoint of economic, environmental, and societal issues [3]. Biomass is commonly used as carbon source for synthesis of carbonaceous materials by HTC. Biomass is a qualified carbon raw material for the synthesis of valuable carbon materials because it is available in high quality and huge amount, and is an environmental friendly renewable resource. To date, most of the carbon materials prepared by HTC using biomass limit to functional carbonaceous materials, such as carbon sphere [4, 5], nanofiber [6], core-shell structure [7], and so on. As far as we are aware, fabrication of C/C composites by HTC using biomass has never been reported earlier. In this study, we report the C/C composites synthesized by HTC using starch as the carbon source. The microstructure and mechanical properties of the obtained composites were studied.

2. Experiments

A needle punched carbon felt with a bulk density of 0.4 g/cm^3 was used as preform, which were purchased from the YiXing Tianniao Hight Technology Co ., Ltd. The felts were made up of layers of non-woven carbon fiber cloth and short-cut web after needle-punching step by step. The carbon fiber type of the felts was T300 PAN-based carbon fiber. The received carbon felt was cut into rectangular cuboids with dimension of 10×20×40 mm. Starch soluble (Chemically Pure) was employed as the carbon source, which was purchased from the Aladdin industrial corporation. The starch soluble was dissolved in water with a concentration of 54 g/L. A typical cycle of the hydrothermal carbonization process is as follows. Firstly, the cut carbon felt was put into a 100 ml Teflon autoclave and immersed with 50 ml starch solution. Subsequently, the Teflon autoclave was sealed and heated by a microwave accelerated reaction system (MARS-10, SINEO) with a frequency of 2450 MHz and output of 400 W. The heating of the autoclave was performed as follow: (i) heating to 200 ^{o}C with a heating rate of 10 ^{o}C/min; (ii) holding at 200 ^{o}C for 120 min; (iii) free-cooling to room temperature. In the temperature holding process, the pressure maintains at 2.0 MPa in the hydrothermal system. Then, the carbon felt was takeout from the cooled autoclave and washed in water to remove the attached materials. Finally, the carbon felt was dried at 80 ^{o}C for 6 hours. The weight of the treated carbon felt was recorded. The similar process was carried out for 10 cycles to get the densified C/C composites.

XRD measurements were performed on a Panalytical X-Pert Pro diffractometer with CuKa monochromatic radiation (k=1.5406Å). Raman spectra were recorded on a Renishaw RM2000 microspectrometer with 514.5 nm laser excitation. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Bruker EQUINOX 55 spectrometer. Scanning electron microscopy (SEM) images were taken on a JEOL 6390 instrument in vacuum. The sample was coated with platinum before SEM analytical. Flexural strength and flexural elastic modulus of the composites were measured using the three-point bending test with a span of 30 mm.

3. Results and discussion

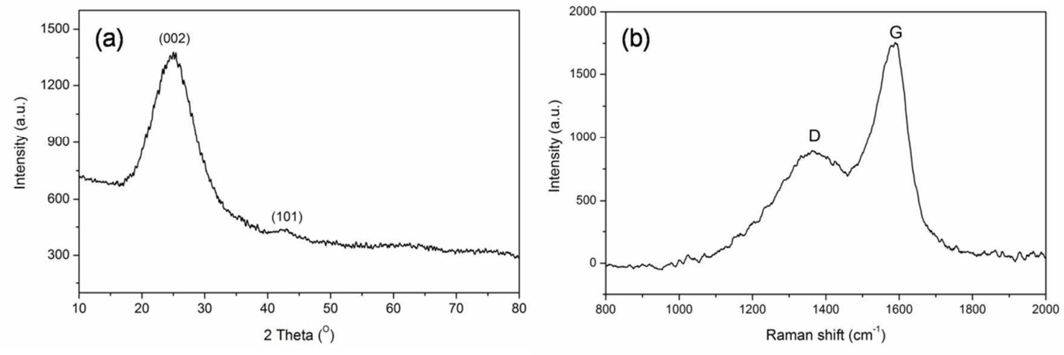

Fig. 1 XRD pattern (a) and Raman spectra (b) of the prepared C/C composites.

Fig. 1(a) shows the XRD patterns of the prepared samples. The peaks at approximately 25.3 ° and 42 ° correspond to (002) and (101) plane of carbon. The broadening and left-shift of these peaks suggests the presence of an amorphous carbon phase in the prepared C/C composites. Raman spectrum was used to further analyze the structure of the carbon matrix, as shown in Fig. 1(b). The Raman spectrum shows two bands at 1580 and 1353 cm^{-1}, corresponding to the E_{2g} vibration mode of the graphite layers (G-band) and the A_{1g} mode for the disordered graphite structures (D-band), respectively. It is well known that the graphitic degree of carbons is confirmed by the width of I_G peak and the value of I_D/I_G. The I_D/I_G value of carbon matrix is 0.61 which indicates that the carbon matrix is mostly composed of amorphous structure. The XRD and Raman results show that the obtained carbonaceous matrix is an amorphous carbon, which is similar to the carbon sphere obtained by HTC of glucose [8].

Fig. 2 shows the FT-IR spectra of the prepared samples. The wide band between 3000 and 3700 cm^{-1} is assigned to the stretching vibrations of O-H (hydroxyl or carboxyl), and the bands around 2800-3000 cm^{-1} are the characteristic stretching vibrations of aliphatic C-H [9]. The absorption bands at 1698 and 1622 cm^{-1} are attributed to C-O and C=C vibrations, suggesting the aromatization of the samples during the hydrothermal treatment. The bands at 1138 cm^{-1} correspond to C-O (hydroxyl, ester or ether) stretching. These results suggest that functional groups mainly containing -OH and C=O were produced on C/C composites, which are common for the carbonaceous materials prepared by HTC [10].

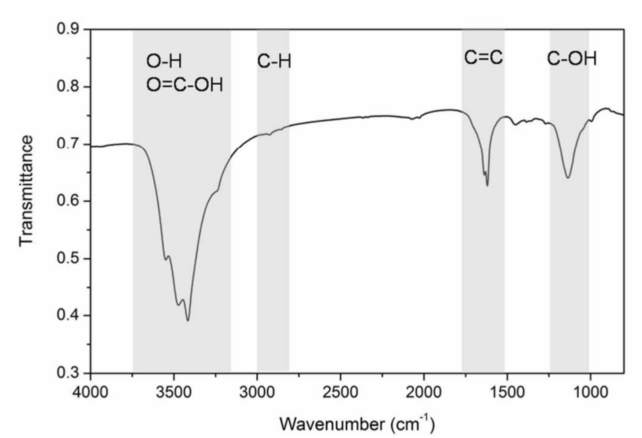

Fig. 2 FT-IR spectra of the matrix carbon in the prepared C/C composites

Fig.3 (a) shows the variation of the composites density with the HTC time. In the initial cycles of the HTC treatment, the density of the composites increases rapidly. With 4 cycles (8 hours) of HTC treatment, the density of the composites reaches about 1.0 g/cm^3. After 10 cycles (20 hours) HTC treatment, the density of composites reaches 1.23 g/cm^3. The open porosity of the C/C composites is 10.9%. These results suggest that HTC is an efficient way for the densification of the C/C composites. The C/C composites prepared by HTC are lighter than the one prepared by CVI, suggesting the density of the HTC carbon is smaller than that of the pyrolytic carbon. Measured by the Archimedes principle, the density of the HTC carbon is about 1.25 g/cm^3. Fig.3 (b) shows the morphology of the composites after 20 h HTC treatment. Carbonaceous materials fill up the narrow interspaces among the fibers and make the composites dense.

The carbon matrix in intimated contact with the carbon fiber suggests the carbon precursor is able to wet the surfaces of the carbon fiber during the HTC process.

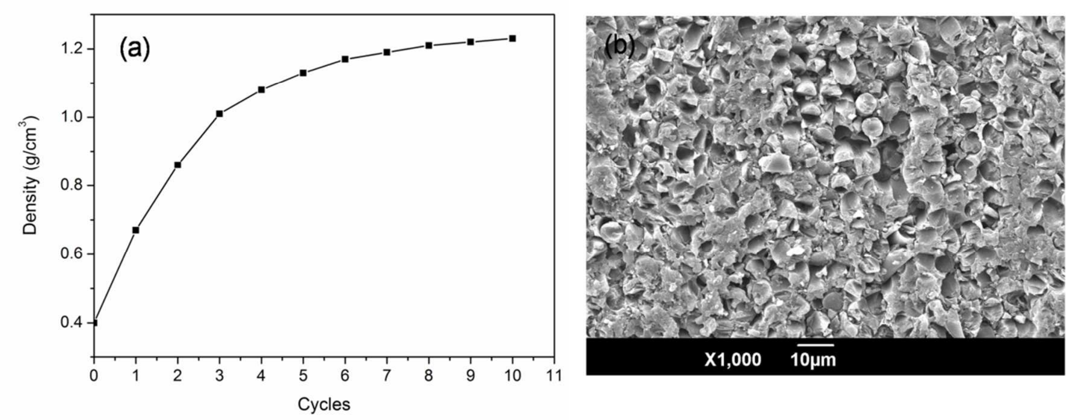

Fig. 3 Variation of the density of the composites with the HTC time (a), and microstructure of the prepared C/C composites (b).

Fig.4 (a) shows the load-displacement curves of the composite during flexural test. The fracture of the composites presents a typical pseudo-plastic fracture characterization. An elastic deformation at first occurs under flexural load, and the curve on this stage shows a linear relationship between the strain and the load. Then the deformation transfers to a plastic deformation stage. Meanwhile, the flexural load reaches its maximum and then a stepwise failure occurs. Fiber pull-out can be seen in the fracture surface of the C/C composites, as shown in Fig.4 (b). The surface of the pull-out fiber is rough, suggesting a good bonding between fiber and matrix. The flexural strength and modulus of the composites can reach 146 MPa and 9.6 GPa, respectively. The flexural strength of the C/C composites prepared by HTC is similar to that of the C/C composites prepared by CVI [11, 12]. However, the flexural modulus is lower than that of the of the C/C composites prepared by CVI [11, 12]. These results suggest that the C/C composites fabricated by HTC using biomass can applied in the engineering field.

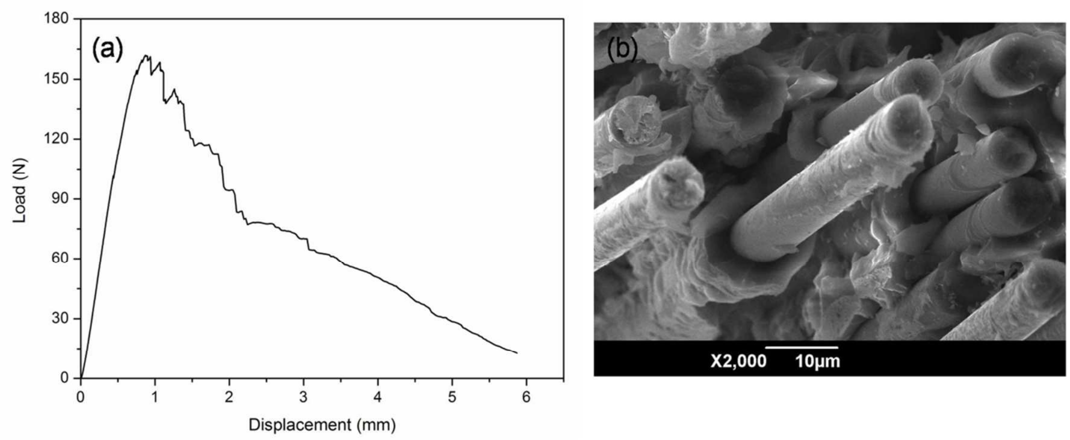

Fig. 4 Load-displacement curves (a) and fracture surface (b) of the prepared composites.

4. Conclusion

We fabricate the C/C composites by HTC technique using starch as carbon source successfully. The C/C composites can be densified by 20 hours HTC treatment and get to 1.23 g/cm^3 with a porosity of 10.9%. The matrix of the C/C composites is an amorphous carbon functionalized with the hydroxyl and carboxyl groups. The flexural strength and modulus of the composites can reach 146 MPa and 9.6 GPa. This confirmed that the novel C/C composites have potential applications prospect, such as bone substitute materials. HTC, as an economic and environmental-friendly technique, is potential for the fabrication of C/C composites.

Acknowledgements: This work has been supported by National Natural Science Foundation of China (Grant No. 51302160), China Postdoctoral Science Foundation (Grant No. 2013M530414), and Natural Science Foundation of Education Department of Shaanxi Provincial (Grant No. 2013JK0938).

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