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Carbon 44 (2006) 1560–1564

CARBON

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A study of the properties of carbon foam reinforced by clay

Xinying Wang [a,*], Jiming Zhong [a], Yimin Wang [b], Mingfang Yu [b]

[a] College of Material Science and Engineering, DongHua University, Shanghai 200051, PR China
[b] State Key Laboratory for Chemical Fiber Modification, Shanghai 200051, PR China

Received 25 August 2005; accepted 16 December 2005
Available online 7 March 2006

Abstract

A novel carbon foam with high strength and very low thermal conductivity was prepared by thermal treating of coal tar based mesophase pitch mixed with montmorillonite clay. SEM observation showed that less micro-cracking appeared on the cell wall of foam by adding of clay-montmorillonite. Foam mechanical properties were improved and its thermal conductivity was markedly decreased. The compressive strengths were increased by 64%, 96% and 100% when the additive amounts of clay were 2%, 5% and 10% (wt%), respectively. Due to the high thermal insulation and lamellar structure of clay, the thermal conductivity of carbon foam decreases from 2 W/m K to 0.25 W/m K.

Keywords: Mesophase pitch; Carbon composites; Coal tar pitch; Thermal conductivity

1. Introduction

Carbon foam as a kind of thermal insulation materials was first reported by Walt Ford in 1960s. Since then, carbon foam has been developed rapidly. In the traditionally preparation method of carbon foam, thermosetting polymers were used as precursors and carbon foam was obtained after pyrolysis, which was known as RVC foam [1]. In 1981, a new method was found by foaming a pitch with blowing agent at high pressure [2]. Both RVC foam and pitch-derived foam need stabilization before carbonization which is time-consuming and high cost. Though, the thermal conductivity of carbon foams mentioned above are very low, the mechanical properties of carbon foam are however quite poor. Novel carbon foam with thermal conductivity ranging from 0.3 W/m K to 150 W/m K was prepared from naphthalene based mesophase pitch (of Mitsubishi Gas Co. Ltd) at Oak Ridge National Laboratory (ORNL) [3]. The compressive strength of RVC is only 0.76 MPa. In this study, carbon foam is made from coal tar based mesophase pitch and reinforced with clay-montmorillonite. The excellent thermal stabilization and thermal insulation of clay endow carbon foam with low thermal conductivity significantly. Because of the laminar structure of clay, it is easy to form disk-like structure of liquid crystal polymer in mesophase pitch, which leads to good compatibility of clay and mesophase pitch. In addition, the mesophase pitch can be carbonized between the layers of clay and its growth of crystalline is confined and forms two-dimensional turbostratic structures. As a result, the imperfections of carbon foam such as micro-cracking are reduced greatly and the mechanical properties of carbon foam are therefore improved. In this paper, the mechanical properties and thermal conductivity of carbon foam with and without clay are compared and discussed in detail.

2. Experimental

2.1. Preparation of mesophase pitch

The coal tar based mesophase pitch (CTP) is prepared as following. The clay-montmorillonite was pretreated with alkylamine to produce Na-montmorillonite. The

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[*] Corresponding author. Fax: +86 21 62379309.
E-mail address: wxy9441@163.com (X. Wang).

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doi:10.1016/j.carbon.2005.12.025

Table 1
The properties of mesophase pitch

Sample	Clay/%	Carbon yield/%	Soften point/°C	Quinine Insoluble/%	Mesophase content/%
CTP0	0	95.0	275	45	95
CTP2	2	90.5	290	67	93
CTP5	5	90.3	300	69	88
CTP10	10	82.5	330	68	87

as-received pitch is mixed with pretreated Na-montmorillonite clay and pyrolyzed at a temperature of 400–450 °C for 2–6 h with sparging of nitrogen. The properties of the resultant mesophase pitch are listed in Table 1. CTP0, CTP2, CTP5 and CTP10 represent CTP with addition of 0%, 2%, 5% and 10% clay, respectively.

2.2. Preparation of foam

The mesophase pitch obtained is pulverized into granules of diameter <0.1 mm and fed into a mold. The mold is set in a high temperature and pressure chamber. The high pressure and temperature chamber is evacuated below 0.01 MPa. The air in the chamber is replaced with nitrogen. The pressure reaches to 8 MPa when the temperature rises to 500 °C and is maintained in this condition for 1–4 h. Finally the chamber was turn off and cooled down to room temperature. The carbonization is performed at 1200 °C at heating rate of 2 °C/min under nitrogen flow and kept for 3 h. The carbon foams derived from CTP0, CTP2, CTP5 and CTP10 are marked as CTF0, CTF2, CTF5 and CTF10, respectively.

2.3. Compressive test

The size of cubic sample is 10 × 10 × 10 mm. The monotonous compressive test is performed on two different directions of foam because the mechanical properties of foam are related to the direction of foam growths.

2.4. The microstructure of foam

SEM was used to observe the microstructure of carbon foam. X-ray diffractometer is used to study the crystal structure. The radiation is Cu K_α of 40 KV, 40 mA and the scanning 2θ is from 5° to 50° at the speed of 2°/min.

2.5. The thermal conductivity

The test of thermal conductivity is performed with a xenon flash diffusivity technique at room temperature. The size of sample is 10 × 10 × 5 mm.

3. Results and discussion

3.1. The compressive strength of carbon foam

The coal tar mesophase pitch with different amount of clay is foamed with same process. The initial pressure is 4 MPa and final pressure reaches 8 MPa within 2 h of soaking time for foaming. The corresponding properties of foam are listed in Table 2. The compressive strength is showed in Fig. 1. The ultimate compressive strengths of carbon foam are 10.2 MPa, 12 MPa and 12.8 MPa when the additive amount of clay is 2%, 5% and 10% (wt%), respectively. It shows that the compressive strengths of clay-reinforced foam are higher than that of foam without of clay by 46%, 71% and 83%, respectively.

The compressive strain of carbon foam without clay is 7.5%, while the ultimate compressive strains of carbon foam with 2%, 5% and 10% (wt%) of clay are 1.72%, 2.8%, and 9.4%, respectively. When the clay content is 0%, the compressive strength is low and strain is high. Moreover, a plateau region appears on the S–S curve of foam without clay, indicating that many type of imperfection exist in the foam. Stress concentrations result from imperfections lead to the disruption of carbon foam at different stage. When the additive amount of clay is 10%, the curve becomes similar to that of foam without clay, i.e., the

Table 2
The properties of carbon foam with different additive amount of clay

Foam	CTF0	CTF2	CTF5	CTF10
Clay/%	0	2	5	10
Apparent density/g/cm^3	0.727	0.73	0.61	0.71
Porosity/%	75	63	57	45
Opening/%	94.05	93.91	93.52	75.04
Thermal conductivity/W/m K	2	0.5	0.36	0.25

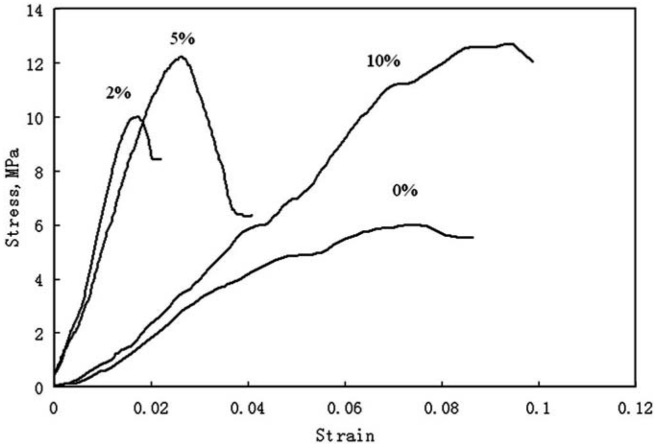

Fig. 1. The compressive strength vs strain of carbon foam with different amount of clay.

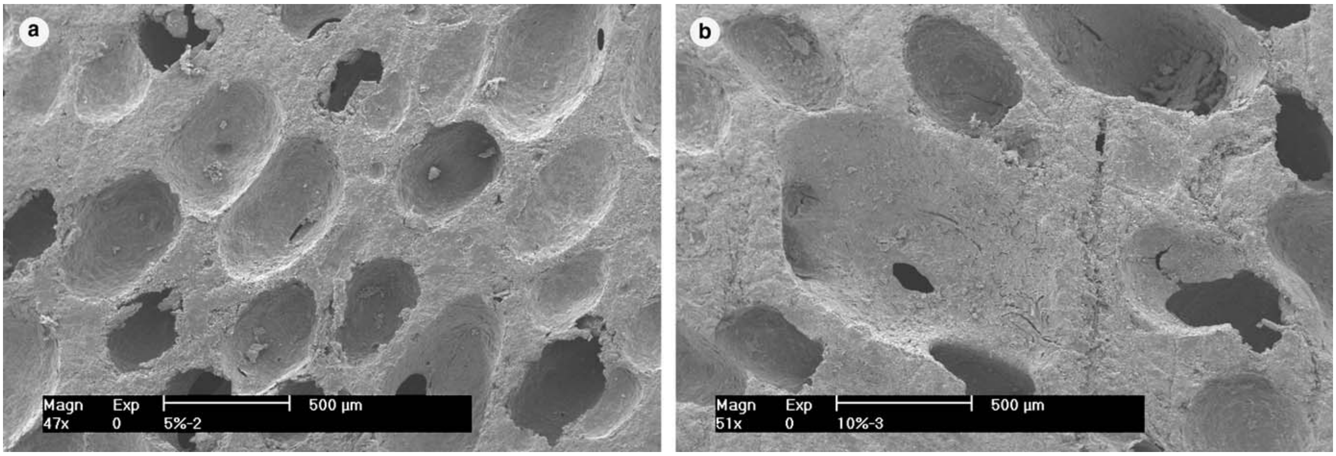

Fig. 2. The SEM of carbon foam with (a) 5% of clay and 10% of clay (b).

high strain and the plateau region. SEM images of carbon foam with 5% and 10% of clay are shown in Fig. 2. It illustrates the inhomogeneous pore of foam with 10% of clay and that with 5% of clay. High content of clay (>5%) causes the rising of pitch viscosity and soften point, as high as 330 °C. As a result, it is difficult for the pitch to flow freely during the foaming above its soften point and the foam pore is inhomogeneous. The serious problem brought by the high content of clay is that the thickness of cell wall of carbon foam becomes uneven and the imperfections are increased (Fig. 2(b)). This will certainly lead foam to be disrupted at a wide range of strain. The disruption of foam with 10% of clay begins at 0.04 of strain and its compressive strength is only 6 MPa. Summarily, in order to improve the compressive strength of foam, the additive amount of clay should be below 10% and range from 2% to 5% (wt%). The mechanical properties of foam will be reduced when the content of clay is higher than 5%.

3.2. The microstructure of carbon foam

The micro-cracking of carbonized foam is observed by SEM. The SEM observations of carbon foam with different content of clay after carbonization are shown in Figs. 3 and 4. After carbonization, the cross-section morphology of foam is changed. A large amount of micro-cracks appeared on the cell wall of foam without clay and very few appeared on the foam cell wall with clay. On the wall of foam without clay, the micro-cracking is parallel to each other along the cell wall. The micro-cracking shows a broad and long morphology and appears on almost whole wall of the cell (Fig. 3). As for foam with clay, the micro-cracking is far less and most of cells are integrated without being destructed (Fig. 4). The high temperature treatment contributes not only to remove hydrogen and heteroatom but also to the crystal orientation. The shrinkage of foam occurs due to the reduction of foam interlayer spacing and the increase in real density [4]. The foam mechanical

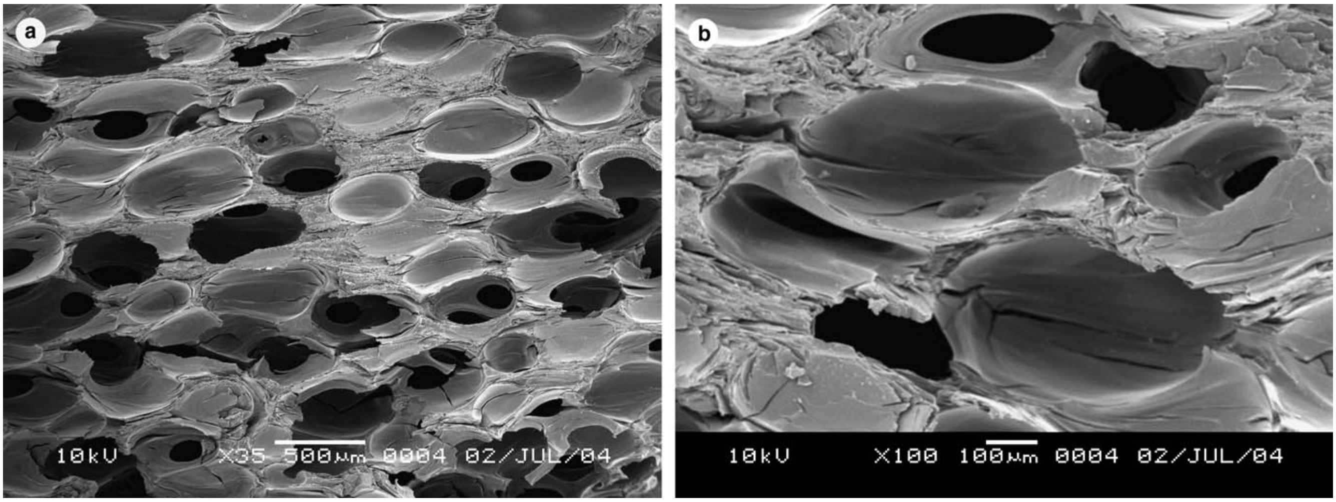

Fig. 3. SEM of foam without clay: (a) the observe of carbon foam, (b) the micro-cracking on cell wall.

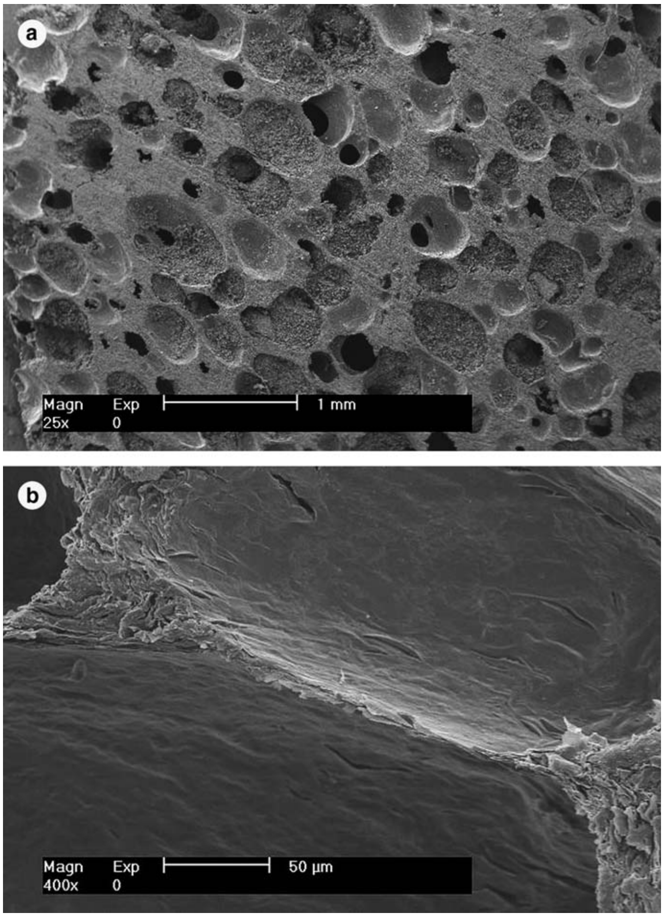

Fig. 4. SEM of foam with 5% (wt%) of clay: (a) the observe of carbon foam, (b) The micro-cracking on cell wall.

properties and thermal conductivity will be decreased with the developing of cracking. The structure of clay is laminar and can be comparable with the disk-like mesophase domain very well during the production of foam at high temperature. X-ray results are shown in Table 3. Since clay is a kind of 2:1 laminar mineral [5], the high activity and distance between clay layers offer an excellent place for the formation of sandwich structure of polymer chain and clay layers. After carbonization, two-dimensional turbostratic structure other than three-dimensional structure is formed due to the confine of clay laminar. The two-dimensional layers are tightly stacked. The crystalline spacing of mesophase pitch with clay is decreased from 3.519 Å to 3.473 Å. The densely packed structure will reduce the shrinkage of foam during the heat treatment and result in the decrease of micro-cracking. As a result, the mechanical properties will be improved by the reduction of micro-cracking and laminar clay will benefit the reduction of carbon foam thermal conductivity as well.

Table 3
The crystalline lattice indices

Pitch	Interlayer spacing (dm/Å)	Stack height (Lc/Å)	Crystal size (La/Å)
CTP0	3.519	33.62	10.77
CTP2	3.485	37.31	11.58
CTP5	3.473	44.12	15.06
CTP10	3.517	30.15	9.36

3.3. The thermal conductivity of carbon foam

The thermal conductivities of carbon foams with different amounts of clay are listed in Table 2. The thermal conductivity of carbon foam without clay is about 2 W/m K. However the thermal conductivity can be decreased significantly from 0.5 W/m K to 0.25 W/m K when the amount of clay varies from 2% to 10%. The structure of mesophase pitch will be changed to disk like laminar by heat treatment. When the heating temperature is lower than 1200 °C, the structure of carbon foam is turbostratic structure where the laminas are randomly existed in carbon foam. The high activity and distance between layers of clay offer an excellent place for the formation of sandwich structure of polymer chain with clay layers. After heat treatment, two-dimensional turbostratic structure other than three-dimensional structure is formed due to the limitation of clay lamina. The two-dimensional layers are stacked tightly and randomly. The turbostratic structure and complicated pore path of carbon foam induced by the clay can obstruct the conduction of heat and as a result the thermal conductivity of carbon foam can be reduced greatly. In addition, the thermal conductivity of clay is as low as 0.03 W/m K and therefore clay is often used as insulation barrier material in many applications [5].

Table 2 shows the porosity and opening of foams with and without clay. The decrease of porosity and opening with the increase of clay indicates the increase of amount of close pore. On the other hand, the addition of clay will increase the viscosity of mesophase pitch during the foaming and this will confine the growth of pore completely. As a result, the porosity and open pore percentage decrease accordingly. The increase of close pore also makes the path of heat diffuse circuitous and improves thermal insulation of carbon foam.

4. Conclusions

In this study, high strength, low thermal conductivity carbon foam reinforced by clay is produced from coal tar based mesophase pitch. SEM and X-ray show that less micro-crackings appear on the foam cell wall and the crystal spacing of mesophase pitch with clay is decreased from 3.52 Å to 3.47 Å. The densely packed structure will reduce the shrinkage of foam during heat treatment and result in the decrease of micro-cracking. As a result, the mechanical properties will be improved by the reduction of micro-cracking and laminar clay will benefit the reduction of carbon foam thermal conductivity as well.

Carbon foam mechanical properties and thermal insulation can be improved by the adding of clay. The compressive strength is increased to 10.2 MPa, 12 MPa and 12.8 MPa from 6.1 MPa when the additive amount of clay is 2%, 5% and 10%, respectively. Due to the high thermal insulation of laminar clay structure, two-dimensional turbostratic structure of carbon foam is formed and the thermal conductivity of carbon foam decreases from 2 W/m K to 0.25 W/m K.

Acknowledgements

This work is financially supported by Science and Technology Commission of Shanghai Municipality (No. 03JC14010). The authors are grateful to the assistance of Jing Tian and Changxing Zhang.

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