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Preparation and characterization of carbon foams with high mechanical strength using modified coal tar pitches

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ABSTRACT

Carbon foams with high mechanical strength were prepared using coal tar pitches modified with cinnamaldehyde (CMA) and boric acid, via pretreatment, foaming and carbonization process. The properties of modified pitches, pretreatment pitches and resultant carbon foams were studied by Fourier transform infrared spectroscopy (FTIR), optical microscope, thermogravimetry analyzer, X-ray diffractometer (XRD), scanning electron microscope (SEM) and universal testing machine, respectively. Results show that the chemical composition and softening points of pitches are adjusted by modification with different amount of CMA, as well as the morphology and properties of pretreatment pitches. The relation between the properties of modified coal tar pitches and the structure of resultant carbon foams is also investigated. Investigation indicates that the composition and softening point of pitches have a significant impact on the morphology and properties of resultant carbon foams. Moreover, the mechanical strength of carbon foam is also improved via modification of pitches and the highest mechanical strength reaches to 21.27 MPa when the additive amount of CMA is 7 wt%.

1. Introduction

Carbon foams have attracted considerable attention in the past decades, due to their special features, such as lightweight, high mechanical strength, refractory, adjustable thermal conductivity and electrical conductivity [1–6]. Potential applications of carbon foams are manifold, such as heat exchangers, high-temperature thermal insulation, electromagnetic shielding, electrodes for fuel cells, catalyst support, radar absorption, filters, etc. [7–11]. Initially, carbon foams were obtained by carbonization of polymeric foams. This kind of carbon foam has limited mechanical strength although it possesses uniform reticulated structure [12,13]. Moreover, the synthesis of carbon foam could also be achieved using coal tar pitch. This method is economical and the resultant carbon foam shows better mechanical strength [14–16].

Coal tar pitch is a kind of excellent precursor for synthesizing carbon foam because of its high carbon content, good fluidity, easy graphitization and low cost [17–19]. Generally, the chemical composition of commercial coal tar pitch is complex, which mainly includes diverse polycyclic aromatic hydrocarbon (PAH) and its ramification. Although the carbon foam derived from coal tar pitch has certain mechanical strength, it is still not satisfied enough for specific application. Recently, several literatures reveal that the structure of carbon foam mainly depends on the properties of foaming precursor [20–22]. This means that it is possible to obtain carbon foam with desired structure and properties via adjusting the properties of foaming precursor. For instance, Tsyntsarski and coworkers [23] synthesized carbon foam using precursors obtained after thermo-oxidation treatment of commercial coal tar pitch with H_2SO_4 and HNO_3. The relation between the properties of the precursor and the structure of obtained foam was investigated. The results indicate that the properties of coal tar pitch can affect the foaming process and foam structure. Moreover, the properties of modified pitches allow foam formation at lower pressure. However, few works have been carried out to improve the mechanical strength of carbon foam via modifying precursor.

Cinnamaldehyde (CMA) is frequently used as cross-linking agent [24], and its aldehyde group can react with the small molecule of coal tar pitch to form large molecules under the condition of acid catalyst [25]. Hence, the present study selects CMA as treatment reagent to modify coal tar pitches in the presence of boric acid. Then the modified coal tar pitches are used as precursor for preparing carbon foams. The relation between the chemical composition and physical properties of modified coal tar pitches and the properties of obtained carbon foams is disclosed in the present

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Table 1
General properties of parent coal tar pitch.

SP[a] (°C)	QI[b] (wt%)	TI[c] (wt%)	C/H	Carbon yield (wt%)
120	7.9	44.05	1.9	57.75

[a] Softening point.
[b] Quinoline insoluble.
[c] Toluene insoluble.

work. The main purpose of our study is obtaining carbon foams with high mechanical strength using this modification.

2. Experimental

2.1. Raw materials

The parent material used in this work is commercial coal tar pitch with a softening point of 120 °C supplied by Wuhan Steel Co. Ltd. (Wuhan, China). The specific properties are listed in Table 1.

2.2. Pitch modification

100 g coal tar pitch powder and 3 g boric acid were mixed in a round bottom three-neck flask. After heating the mixture up to 100 °C, CMA was added slowly with continuous stirring. Then the mixture was heated up to 150 °C with soaking time of 3 h. The whole modification process was achieved under a N_2 flow of 50 ml min^{-1}. Additionally, the additive amount of CMA was 0 wt%, 3 wt%, 7 wt%, 10 wt% and 13 wt%, respectively. For simplicity, the modified pitches were denoted as CTP1–CTP5.

2.3. Pretreatment of pitches

Generally, pitches need preliminary treatment before foaming process. The pretreatment usually transforms pitches into mesophase pitches, which have good fluidity properties meeting for the foaming requirements. In order to obtaining mesophase pitches, CTP1–CTP5 (ground to ~100 μm) were heated up to 420 °C (heating rate 1.5 °C/min) for 4 h in a N_2 atmosphere, respectively.

2.4. Foaming method and carbonization process

The foaming process was carried out in a stainless autoclave. Pretreatment pitches were heated up to 500 °C (heating rate 1.5 °C/min) for 2 h in a N_2 atmosphere at pressure up to 3 MPa. Then the resultant green foams were transferred to carbonization furnace and were heated up to 800 °C in a N_2 atmosphere for 2 h.

2.5. Pitches characterization

The detailed measurement of TI content, QI content, SP and CV were introduced in [26]. FTIR spectra of pitches were obtained using a Prestige-21 FTIR spectrometer. The testing range is between 500 cm^{-1} and 4000 cm^{-1}. The optical structure of pretreatment pitches was observed using an OLYPUMS-B061 optical microscope with cross-polarized light. A TG-SDTA851 thermogravimeter analyzer was employed to measure the weight loss of pitches as a function of temperature from 50 °C to 800 °C (heating rate 10 °C/min).

2.6. Carbon foams characterization

X-ray diffractometer (XRD-7000) using CuKα radiation (λ = 0.15406 nm) was employed to analyze the crystal structure of carbon foams. The X-ray diffraction patterns were recorded in the angular range of 15–80° with a step size of 0.02°. A JSM-6700 Field-emission scanning electron microscope was also used to observe the morphology of obtained samples. The bulk density of carbon foams was determined from the values of the weight and the volume.

Table 2
Properties of modified pitches.

Sample	QI[a] (wt%)	TI[b] (wt%)	SP[c] (°C)	Carbon yield (wt%)
CTP1	7.9	44.05	120	57.75
CTP2	13.78	33.03	106	62.14
CTP3	13.82	35.87	102	63.92
CTP4	13.35	37.05	95	63.51
CTP5	13.59	33.71	91	63.24

[a] Quinoline insoluble.
[b] Toluene insoluble.
[c] Softening point.

Moreover, compression strength test was performed on a universal testing machine (Instron 3382) at room temperature. Sample (15 mm in diameter and 15 mm in height) was compressed between two stainless platens with a crosshead speed of 5 mm/min. And the compressive yield strength (σ) was calculated by

$$\sigma = \frac{F}{A} \tag{1}$$

where F is the load at yield, A is the cross-section area.

3. Results and discussion

3.1. Modification and pretreatment

3.1.1. Properties of modified pitches

During the foaming process of preparing carbon foam using coal tar pitch, the evolving volatiles from the light compounds and the thermally decomposed fractions serve as "bubble agents" to generate foam cells in molten pitches, meanwhile the volume of foaming pitches increases [27–29]. Therefore, the viscosity and volume swelling of the foaming precursors at the foaming temperature are two key factors that affect the foaming and cell structure. In the present study, the chemical composition and softening point of pitches, which are related to the viscosity and volume swelling, are used as main factors which influence the foam cell structure.

Table 2 lists the main properties of parent and modified pitches CTP1–CTP5. It can be seen that CTP1 contains low percentages of primary QI content, which is a component of commercial coal tar pitch. However, the QI content increases after modification. On the one hand, the polycondensation and polymerization reaction among PAH can form QI large molecules. On the other hand, the reaction between the aldehyde group of CMA and the small molecules also form QI large molecules. Meanwhile, the heat treatment during the modification process improves the thermal stability of pitches, and hence reduces the weight loss of pitches.

The TI content of pitches is related to the extent of polycondensation reaction. And the data in Table 2 also shows that the TI content reduces after modification. This means a certain amount of TI content transforms into soluble fractions due to the modification by CMA and boric acid. Additionally, the softening point of modified pitches reduces as the increase of the addition amount of CMA.

3.1.2. FTIR analysis of modified pitches

For better understanding the structure of modified pitches, Fourier transform infrared spectroscopy has been employed to identify functional groups. Fig. 1 shows FTIR spectra of parent and modified pitches. The absorption in the range 700–900 cm^{-1} is assigned to the out-of-plane vibration of aromatic C—H in the aromatic structures. And those absorption peaks decreases because