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Co-carbonization behavior of petroleum pitch/graphene oxide: Influence on structure and mechanical property of resultant cokes

Youliang Cheng, Lu Yang, Changqing Fang*, Xue Guo

Faculty of Printing, Packaging Engineering and Digital Media Technology, Xi'an University of Technology, Xi'an 710048, PR China

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ABSTRACT

By adding graphene oxide (GO) into petroleum pitch, mesophase pitch/GO composites were obtained via liquid dispersion and co-carbonization method. The results show that the mesophase development of the petroleum pitch/GO mixture was obviously changed during the heat treatment and the anisotropic texture was flow domain when the GO content was 0.03 wt%. The interlayer spacing of the heat treatment products was reduced firstly, and then increased with increasing GO content. Moreover, the thermal stability of the precursor of mesophase pitch/GO composites is higher than that of the heat treatment product of the petroleum pitch. The mass ratio of GO to the petroleum pitch plays an important role in the mechanical properties of the composites. The bending strength of the mesopahse pitch/GO composites first increased and then decreased with the increase of the proportion of GO. When the GO content was 0.03 wt%, the bending strength of the composites reached to the maximum of 81.5 MPa.

1. Introduction

Petroleum pitch is a complex mixture of condensed aromatic hydrocarbons and heterocyclic compounds, which confer the blending property with other material [1]. Mesophase pitch can be formed during the co-carbonization of petroleum pitch via the thermal polymerization reaction [2]. Due to its outstanding thermal stability, high thermal conductivity and excellent conductivity [3], mesophase pitches are widely used as the precursors of carbon fibers [4,5], carbon foam [6,7] and carbon-carbon composites [8]. However, there are some drawbacks in the application of petroleum pitch as the result of the emission of polycyclic aromatic hydrocarbons during the pyrolysis [9], such as a low carbon yield and poor mechanical properties.

In order to improve the mechanical properties of the carbonization product of the petroleum pitch, it is necessary to blend the petroleum pitch with the reinforcing materials. Graphene oxide can be selected the promising reinforcing material due to its unique structure and excellent mechanical properties [10]. Moreover, there are many functional groups existing on the surface of GO, which can promote the affinity of the reinforcing material and the organic matrix materials [11–15]. GO can be used as the co-carbonization agent to change the formation of mesophase pitch during the carbonization [16]. Furthermore, graphite nanoplatelet can exhibit a positive effect on the thermal conductivities and mechanical properties of the nanocomposites [17,18]. Therefore, the petroleum pitch blended with appropriate GO has widely potential applications in the desired precursors of carbon materials.

There were some works suggesting that heat treatment of the pitch with polymers was primarily aimed at preparing modified asphalt and carbon materials [19–22]. Rocha pointed out different additives could accelerate the formation of the mesophase pitch and influence its structure [23]. However, few researches have been given to investigate the influence of the addition of GO on the property of the cokes.

Therefore, the mesophase pitch/GO composites are obtained via co-carbonization in this paper, then the influences of GO on the structure, morphology, thermal and mechanical property of the composites are analyzed and discussed. The purpose of this study is to together take advantage of the excellent properties of GO and the petroleum pitch.

2. Experimental

2.1. Raw materials

NO.90A petroleum pitch was provided from Xi'an Petrochemical Controlled Company and its properties are showed in Table 1. GO was prepared by using the modified Hummers-Offeman's method

* Corresponding author.
E-mail address: fcqxaut@163.com (C. Fang).

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Table 1
Properties of petroleum pitch.

C/H	TI (wt%)	QI (wt%)	SP(°C)
0.73	13.60	0.10	51

Note: C/H: atomic ratio, TI: toluene insoluble, QI: quinolone insoluble, SP: softening point.

[24,25]. The thickness of GO is about 1.0 nm, and the layer number is 1–2 (as shown in Fig. S1).

2.2. Co-carbonization of petroleum pitch/GO

2.2.1. Preparation of the mixture of the petroleum pitch/GO

Petroleum pitch was dissolved in *N*, *N*-Dimethylformamide (DMF) to obtain petroleum pitch solution by filtering, and graphite oxide was dissolved in DMF solution by using ultrasonic method. Then GO were introduced into petroleum pitch solution in three flask with stirring, and the mixed solution was treated by using reduced pressure distillation method at 160 °C. The rations of GO to petroleum pitch were 0 wt%, 0.015 wt%, 0.03 wt%, 0.045 wt%, 0.06 wt%, respectively. The purpose of this method is to fully remove DMF, and then the petroleum pitch/GO mixture was obtained for reserving.

2.2.2. The heat treatment of the petroleum pitch/GO

The prepared mixtures as described above were loaded into the steel reactor and the reaction system was heated to 420 °C at the rate of 2 °C/min under N_2 atmosphere. The reaction system was naturally cooled to room temperature after holding for 2 h and the pyrolytic products were obtained. The resultant pyrolytic products were labeled as PGO0-420, PGO0.015-420, PGO0.03-420, PGO0.045-420 and PGO0.06-420, respectively.

2.2.3. The preparation of mesophase pitch/GO composite

Ground 8 g pyrolytic products were loaded in a steel mould to molding by pressing. The length and width of molded samples were 60 mm and 20 mm respectively. Theses samples were pre-oxidized at 300 °C holding for 30 min before the carbonization. Then mesophase pitch/GO composites were obtained after the carbonization of these samples at 900 °C (a heating rate of 3 °C/min from room temperature to 900 °C) holding for 2 h under N_2 atmosphere. The carbonization products were labeled as PGO0-420-900, PGO0.015-420-900, PGO0.03-420-900, PGO0.045-420-900 and PGO0.06-420-900, respectively.

2.3. Characterization

2.3.1. Morphology analysis

The optical anisotropy images of the pyrolytic products were observed by using polarized microscopy (10XB-PC). The pyrolytic products were placed in the paper moulds. The dental base acrylic resin powders were injected and then methyl methacrylate was added for curing. Finally, the samples were observed under a polarized microscope after grinding and polishing. Fractured micrographs and surface morphologies of the composites were observed by using a SU-8010 scanning electron microscopy (SEM).

2.3.2. Infrared spectroscopy

Fourier transform infrared spectra (FTIR) were obtained by using a FTIR-8400S spectrometer at a resolution of 0.2 cm^{-1}, and the scan range was from 400 to 4000 cm^{-1}. The KBr discs were prepared from the dried mixtures of 1 mg sample and 100 mg KBr.

2.3.3. X-ray diffraction

X-ray diffraction (XRD) tests were performed on an X'Pert High-Score diffractometer (XRD-7000, Japan) with Cu Kα radiation (λ= 0.1541 nm). The L_c and the d_{002} were calculated according to the Formulas (1) and (2), where d_{002} is the interlayer spacing, L_c is the crystallite size, λ is the X-ray wavelength, θ_{002} is the diffraction angle and β_{002} is the half-height width of the diffraction peak.

$$Lc = 0.89\lambda/\beta_{002}\cos\theta_{002} \quad (1)$$

$$d_{002} = \lambda/2\sin\theta_{002} \quad (2)$$

2.3.4. Thermogravimetric analysis

A TF-209 F3 thermogravimetric analysis (TGA) instrument was used to analyze the pyrolytic behavior of the sample from room temperature to 900 °C at a heating rate of 10 °C/min under N_2 atmosphere. The flow rate of N_2 was 100 ml/min.

2.3.5. Raman spectroscopy

Raman spectra were recorded on a HR 800 Horiba JOBIN YVON spectrometer at 514 nm nano-argon in laser. All powder samples were placed on the quartz glass directly in the absence of solvents.

2.3.6. Mechanical property test

Flexural tests were carried out according to ASTM D790 standard by using an Instron1196 universal testing machine, and the strength was evaluated according to the 3-point bending method.

3. Results and discussions

3.1. Morphologies of pyrolytic products

Fig. 1 shows the polarizing micrographs of pyrolytic products obtained from the petroleum pitch with different contents of GO at 420 °C for 2 h. In these micrographs, the brightest part is the anisotropy area, and the content of the mesophase can be determined according to the proportion of the anisotropy area [26]. As shown in Fig. 1a, PGO0-420 shows the mosaic texture and small domain. The reason for this is that the mesophase microcrystal formed during the pyrolysis of green petroleum pitch will grow and aggregate in the liquid phase. Moreover, the content of GO has an important influence on the optical textures of the pyrolytic products. When the GO content is 0.015 wt%, the optical texture is small domains (Fig. 1b). When the GO content increases, the optical textures change to be elongated domains (as shown in Fig. 1c–e). It can be found that the mesophase content (according to the area of anisotropic regions) in the pyrolytic products increases and some holes occur with the proportion of GO increasing. These holes may be caused by the containing oxygen functional groups on the surface of GO which release CO_2 at 420 °C. From evolution of the optical texture, it can be inferred that GO can obviously change the mesophase development of the petroleum pitch during the pyrolysis.

Fig. 2 shows SEM images of the pyrolytic products. It can be seen that the lamellar structure exits in the pyrolytic products. Some mesophase spheres can be observed in Fig. 2a. However, there are no spheres in Fig. 2b and c. The regular lamellar structure can be observed in PGO0.03-420 (as shown in Fig. 2b), and there are some pores in the surface of PGO0.06-420 (as shown in Fig. 2c). These pores may be caused by the release of more light components adsorbed on the surface of excess GO during the heat treatment, and the carbon layer of PGO0.06-420 is loose. It can be inferred that the development of mesophase may be accelerated by GO and the coalescence of mesophase microbeads easily occur form the bulk along the surface of GO. However, excess GO may hinder the stack of the mesophase units in the development stage