Study on carbonization process of coal tar pitch modified thermoplastic phenolic resin

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Abstract: In order to improve the carbon residual ratio of phenolic resin and optimize the structure and properties of its pyrolytic carbon, different quality coal tar pitches are added to the thermoplastic phenolic resin. Thereby, a coal tar pitch modified phenolic resin is obtained. After curing at 220 °C, it is carbonized for 3 h under different conditions and test its carbon residue rate. The structure was characterized by SEM scanning electron microscopy. The results show that: 1) Coal tar pitch modified phenolic resin at a temperature of 900 °C, the heating rate of carbonization is 10 °C/min, and the addition of modifier is 10%, carbonization is the best process conditions for the formation of graphene. 2) Charging is the best process condition for carbon nanotubes formation at a temperature of 1100 °C, a carbonization heating rate of 10 °C/ min, and a modifier addition of 25%.

1. Introduction
Due to the specific molecular structure of the, the properties and applications of phenolic resin are affected. In order to obtain better performance, the most common method at present is to modify the phenolic resin, and the modified material prepared by adding the modifier can improve the thermal stability and carbon residue rate of the common phenolic resin. The application field can be more extensive, and the demand for adhesives, coatings and carbonized materials is huge[2~4]. In order to improve the structure and properties of phenolic resin pyrolysis carbon, Aneziris et al[5~6] and Liu Jun et al[7] combined carbon-containing resin powder (Car-bores) with thermoplastic phenolic resin to form carbon materials, formed after carbonization. The carbon structure of the mosaic structure (anisotropic) greatly improves the thermal shock resistance of the magnesium carbon material. Wu Lin et al[8] used coal tar pitch as a modifier to modify the phenolic resin to explore its solid content and residual carbon value. Based on this experiment, the microstructure of the modified phenolic resin pyrolysis carbon under different carbonization conditions was further explored.

2. Experiment
2.1. Experimental process
After the coal tar pitch is removed from the quinoline insoluble matter, the coal tar pitch is pulverized to a suitable size granule, and the phenolic resin is respectively placed in a four-necked flask with a stirring device and a temperature control device at a certain ratio, first at 60 °C. After the heat is kept
for 40 min and the asphalt is partially melted, stirring is started to uniformly mix the phenolic resin and the asphalt. Then the temperature was freely raised to 90 °C, and reacted at this temperature for 1 h to obtain a modified phenol resin. Then, 2–3 g of resin was placed in the porcelain boat, 10% hexamethylenetetramine was added, stirred uniformly and placed in a 205 °C drying oven for 2 h, and then carbonized in a tube furnace.

The carbonization product was obtained by raising the temperature from 10 °C/min to 900 °C, 1000 °C and 1100 °C from room temperature and holding at this temperature for 3 h, and then naturally dropping to room temperature. Argon gas was used as a protector throughout the process, and the gas flow rate was maintained at 60 mL/min. After observing the microstructure under SEM electron microscopy, the suitable temperature for heat preservation was obtained, and then the carbonization heating rates were kept at 10 °C/min, 20 °C/min, 30 °C/min, and the temperature was maintained for 3 h after the appropriate temperature, and then naturally cooled. The carbonized product was observed by SEM for microstructure.

2.2. Characterization method

(1) Infrared spectroscopy

We took 1–2 g of modified phenolic resin in a 50 mL tube and added a small amount of ethylene glycol to dissolve. The KBr sheet was compressed by spectral pure KBr tableting method, and then a small amount of the dissolved sample was coated on the disposable pipette, and then subjected to infrared spectrum detection, and the scanning range was 400-4000cm⁻¹.

(2) Scanning electron microscope

We took the blocky carbonized product of the appropriate size and placed it on the sample stage. After the sample was prepared, it was sprayed with gold and then placed in the instrument to observe its microstructure.

3. Results and discussion

3.1. Infrared spectroscopy

Figure 1 shows the FT-IR spectra of different coal tar pitch modified phenolic resins and common phenolic resins. It can be seen from Figure 1 that as the amount of coal tar pitch added increases, the intensity of the C-O stretching vibration peak at the aromatic ether bond at 1251 cm⁻¹ gradually decreases until it disappears. This indicates that as the amount of modifier coal tar pitch is gradually increased, the absorption peak of -COOH in the modified phenolic resin is reduced to disappear, which may be because the oxygen atom in the carboxyl group of the phenolic resin has been intersected with the coal tar pitch. The reaction accelerates the formation of macromolecular planes.

![Figure 1. Infrared spectrum of phenolic resin](image-url)
3.2. Scanning electron microscopy analysis

3.2.1. SEM image analysis of thermal decomposition carbon of coal tar pitch phenolic resin at different temperatures. An SEM image of a 10% coal pitch modified phenolic resin sample charred at different temperatures for 3 h is shown in Figure 2.

![SEM image of 10% coal tar pitch modified phenolic resin sample charred at different temperatures](image)

Figure 2. SEM image of 10% coal tar pitch modified phenolic resin sample charred at different temperatures for 3 h: (a) 900 °C (b) 1000 °C (c) 1100 °C

Figure 2a is easy to form a gaseous carbon element at 900 °C carbonization and can form a carbon core on the carbon substrate, and the carbon element grows on its surface, growing a graphene structure, but when the temperature rises to 1000 °C, it is observed that the graphene structure disappears, and the main substances are all vitrified carbon, which indicates that the formed graphene is decomposed at a high temperature, and the generated carbon vapor is insufficient to form carbon nanotubes. Therefore, when the temperature continues to rise to 1100 °C, we observed carbon nanotubes in Figure 2c, which indicates that as the temperature increases, the temperature reaches the temperature requirement for the carbon compound to form a gaseous elemental carbon atom.

3.2.2. Effect of different carbonization heating rates. The carbonization morphology of 10% coal pitch modified phenolic resin at 900 °C at 5 °C/min, 10 °C/min, 20 °C/min under three different conditions is shown in Figure 3.

![SEM photograph of different carbonization heating rates](image)

Figure 3. SEM photograph of different carbonization heating rates of 10% coal tar pitch modified phenolic resin at 900 °C: (a) 5°C/min (b) 10 °C/min (c) 20 °C/min

When the heating rate is low, the gaseous carbon is not easily formed due to the long heating time; when the heating rate is increased, the gaseous carbon can be formed faster and carbon nuclei can be formed on the substrate, and the carbon element is continuously on the surface. Growth, can grow graphene structure; but when the heating rate reaches 20 °C/min, the temperature rise time is too short, the carbon compound forms a small number of carbon cores on the carbon substrate, and can not form a complete graphene structure.

The carbonization morphology of 10% coal tar pitch modified phenolic resin at 1100 °C is 5 °C/min, 10 °C/min, 20 °C/min under three different conditions as shown in Figure 4.
Figure 4. SEM photograph of different carbonization heating rates of 10% coal tar pitch modified phenolic resin at 1100 °C: (a) 5 °C/min (b) 10 °C/min (c) 20 °C/min

The formation of carbon nanotubes also needs to be generated at a suitable heating rate. The excessively slow heating rate may not meet the requirements for the production of carbon nanotubes, resulting in a decrease in the yield of carbon nanotubes. Increasing the rate of temperature increase will accelerate the carbon nanotubes. It is generated, but the too fast heating rate causes the reaction time to be too short, and even carbon nanotubes cannot be formed.

3.2.3. SEM image of modified phenolic resin charcoal with different proportions of coal tar pitch. The morphology of five different proportions of coal tar pitch modified phenolic resin after carbonization at 1100 °C and 10 °C/min is shown in Figure 2.5.

Figure 5. SEM photograph of carbonized coal tar pitch modified resin after carbonization at 1100 °C and 10 °C/min: 5%(a), 10%(b), 15%(c), 20%(d), 25% (e).

As the amount of coal tar pitch is increased, the number of carbon tubes is also increased, presumably because some components of the coal tar pitch and the phenolic resin are more likely to form carbon nanotubes. A suitable modifier for the formation of the carbon nanotube structure is added in an amount of 25%.

4. Conclusion
(1) Coal tar pitch modified phenolic resin is a good process condition for the formation of graphene at a temperature of 900 °C, a carbonization heating rate of 10 °C/min, and a modifier addition amount of 10%; (2) Charring is a better process condition for the formation of carbon nanotubes at a temperature of 1100 °C, a carbonization heating rate of 10 °C/min, and a modifier addition amount of 25%.
References
[1] Xiao J, Wang Y, Liu Y D, L Y Q and Li W 2010 *Carborn*. 29 31-7
[2] Chen Y L, Liu P and Zhu F F 2013 *J. New Building Mater*. 4 75-8
[3] Yao G X, Hou M S, Gao D and Liu X B 2012 *Journal of Jiangsu University*. 33 333-7
[4] Mao L F and Liu Z Z 2012 *FRP/composite*. 2 64-6
[5] Aneziris C G, Borzov D, Ulbricht J, Suren J and Dern H 2004 *Key. Eng. Mater*. Vols 264-268 pp 1767-1770
[6] Aneziris C G, Homola F and Borzov D 2004 *Adv. Eng. Mater*. 6 562 -8.
[7] Liu Jun and Jacob C 2006 *Re. Mater*. 40 256-259 264.
[8] Wu L, Ou Y Z H, Cao S C, Yi D Li, Qin X R and Wang Y 2005 *Chemical Technology*. 4 17- 9.
[9] Zhang W J, Li T H, Lu M, Hou C, Zhang W and Li T 2013 *New carbon Mater* 28 140-5.