

# Synthesis and carbonization of nickel-modified thermoplastic phenolic resin

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**Abstract:** The use of formaldehyde and phenol as raw materials, under the acidic catalyst, the high temperature polymerization produces a thermoplastic phenolic resin. At low temperatures, modified nickel sulfate is added to synthesize Ni-modified thermoplastic phenolic resin, and carbonization is carried out at high temperature. The effects of carbonization temperature, carbonization heating rate and nickel doping amount on the carbonization product are investigated. Experiments have shown that the optimal conditions for the Ni-modified thermoplastic phenolic resin. The molar ratio of formaldehyde to phenol is 0.85, oxalic acid accounts for 2% of the mass of phenol. The reaction temperature is 100° C. The reaction time is 2 h. The molar ratio of iminodiacetic acid to phenol is 0.03, and the molar ratio of nickel sulfate to phenol is 0.04. The combined temperature is 60°C and the chelating time is 40 minutes. The pyrolytic carbon of the nickel modified phenolic resin is characterized by field emission electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The results show that the best carbonization temperature is 10 °C/min at 1100°C for 3 h, and a large number of carbon nanotubes are formed in the pyrolytic carbon.

## 1. Introduction

Phenolic resins are widely used in molding compounds, adhesives, and coatings because of the advantages of low cost, good heat resistance, flame retardancy, less burning fuming, high thermo-hardness, dry strength, and high strength at high temperature[1-3]. Therefore, the introduction of high-bond energy bonds in phenolic hydroxyl groups or methylene species improves its performance. Ordinary phenolic resin can no longer meet the needs of the manufacturer's production. At present, it can improve its heat resistance by modifying the phenolic resin. The ideal carbon nanotubes are composed of multi-layered graphenes, and the lamellar graphene is crimped into a sealed tube body. The end of the carbon nanotubes is equivalent to half a fullerene. There are many methods for the synthesis of carbon nanotubes, such as catalytic cracking, particle or laser evaporation, and catalyst chemical vapor deposition (CVD) arc discharge[4]. According to different preparation methods, the use of carbon nanotubes is also different[5-7]. According to scholars' research[8-10], some carbon fibers can be prepared at high temperatures using metal inorganic salt catalysts and common resins. On this basis, we can develop a new method for preparing carbon nanotubes.



## 2. Experimental part

### 2.1. Preparation of nickel modified phenolic resin

First, a certain amount of heat-melted phenol is added to the four-necked flask, heated and stirred to maintain the stirring speed at 120 r/min, and then the acidic catalyst oxalic acid (2% of the mass of phenol) is added. The temperature of the control system is 70°C. Then formaldehyde is added dropwise with a constant pressure funnel (the molar ratio to phenol is 0.85). After the formaldehyde is added dropwise, the reaction is incubated for 30 min to obtain methylol phenol. The hydroxymethyl phenol is heated to 100°C, and the micro-boiling is kept for 120 minutes. The NaOH solution is used to adjust the pH of the resin intermediate system between 6.5 and 7.5, and iminodiacetic acid (molar ratio to phenol is 0.03) is added. The temperature is maintained for 20 minutes. The temperature is rapidly reduced to 60° C, and nickel sulfate (with phenol) is added to the system. The molar ratio is 0.01 to 0.05), and the temperature is kept for 40 minutes to obtain a water-containing modified phenolic resin, which is heated to 85° C under a degree of vacuum of 0.09 MPa. Stop heating, and ethylene glycol is added to adjust the viscosity of the resin to obtain a nickel-modified phenolic resin(Ni-MPF).

### 2.2. Preparation of Ni-MPF pyrolytic carbon

The prepared nickel modified phenolic resin is taken out 2-3 g, and then put it into a small porcelain boat; add 10% curing agent; place it in a vacuum drying oven for 2h. Then in the tube furnace, under certain process conditions and high-purity argon protection conditions, the pyrolysis of Ni-MPF is obtained.

## 3. Results and discussion

### 3.1. Analysis of solid content and carbon residue results

With the increase of the content of modifier nickel sulfate, both the solid content and the residual carbon content of the resin increase. The growth trend increases quickly at first and then grows slowly. When the molar ratio of nickel sulfate to phenol is greater than 0.04, the growth rate is slow. As the nickel ion content increases, the coordination polymer structure formed with the resin and the chelating agent gradually increases. When the addition amount reaches a certain value, the nickel ion becomes supersaturated. No coordination reaction occurs at this point. However, the inorganic salt of nickel is difficult to evaporate, and excess nickel sulfate will be deposited in the resin. So the solid content and residual carbon value will increase correspondingly at the increase of the amount of nickel ions. Therefore, we can preliminarily judge that the Ni-modified phenolic resin has a maximum solid content and residual carbon value when the content of nickel sulfate is 0.04.

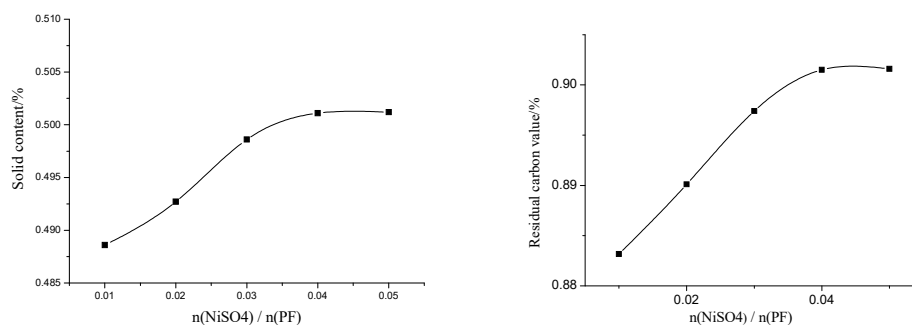


Figure1. Effect of Nickel sulfate addition on resin properties (a) 900°C; (b) 1000°C; (c) 1100°C.

### 3.2. Analysis of infrared results

As can be seen from figure 2,  $1646\text{ cm}^{-1}$  and  $1457\text{ cm}^{-1}$  are carbon-carbon absorption peaks of benzene rings in phenolic resins; The  $\text{C}=\text{O}$  stretching vibration peak of carboxylic acid is about  $1700\text{ cm}^{-1}$ , and the absorption peak of  $\text{C}-\text{O}$  stretching vibration is about  $1300\text{ cm}^{-1}$ . However, these structures do not exist in modified phenolic resins. The newly added peak is  $1646\text{ cm}^{-1}$ , which overlaps with  $1646\text{ cm}^{-1}$  (the area of the peak becomes larger). A new peak is formed at  $1407\text{ cm}^{-1}$ . It can be inferred that the carboxyl group in the iminodiacetic acid forms a coordination structure with  $\text{Ni}^{2+}$ .

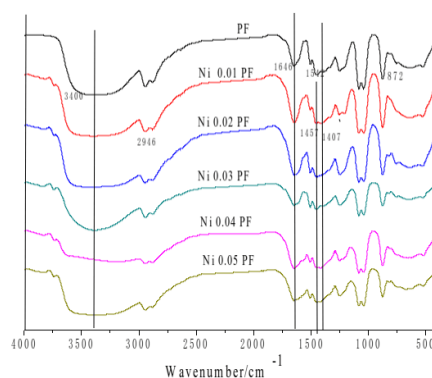


Figure 2. The FT-IR spectra of different concentrations of Ni modified phenolic resin and normal phenolic resin.

### 3.3. Analysis of SEM test results

The SEM image of Ni0.03-PF carbonized at different temperatures for 3 h is shown in figure 3. From the figure 3(a) and 3(b), no structure of highly graphitized carbon nanotubes is found in the nickel-modified phenolic resin carbon carbonized at  $900^{\circ}\text{C}$  and  $1000^{\circ}\text{C}$ . As can be seen from the graph (c), a highly graphitized material having a carbon nanotube structure is formed in the pyrolytic carbon of Ni0.03-PF at  $1100^{\circ}\text{C}$ . At temperatures of  $900^{\circ}\text{C}$  and  $1000^{\circ}\text{C}$ , the temperature at which nickel ions form nickel elements is not reached, and carbon compounds cannot form gaseous single carbon atoms. Therefore, carbon nuclei cannot be formed on the surface of nickel. It shows that nickel has almost no catalytic effect. So there is no carbon nanotube structure in the SEM at  $900^{\circ}\text{C}$  and  $1000^{\circ}\text{C}$ . Through preliminary experiments, we can determine the best carbonization temperature is  $1100^{\circ}\text{C}$ .

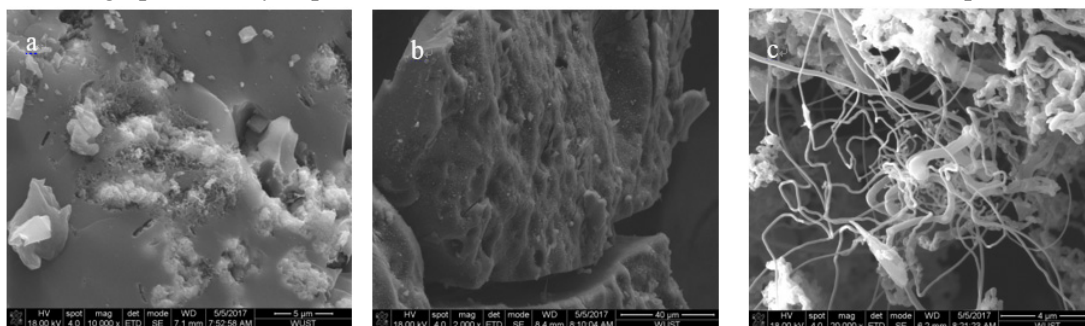


Figure 3. SEM images of Ni0.03-PF samples carbonized at different temperatures for 3h: (a)  $900^{\circ}\text{C}$  (b)  $1000^{\circ}\text{C}$  (c)  $1100^{\circ}\text{C}$ .

At  $1100^{\circ}\text{C}$  and  $10^{\circ}\text{C/min}$ , we chose different samples of  $\text{Ni}_x\text{-PF}$  (where  $x=0.00, 0.01, 0.02, 0.03, 0.04, 0.05$ ). Carbonization was performed in a tube furnace and the product was observed under an electron microscope to obtain an SEM image as shown in figure 4.

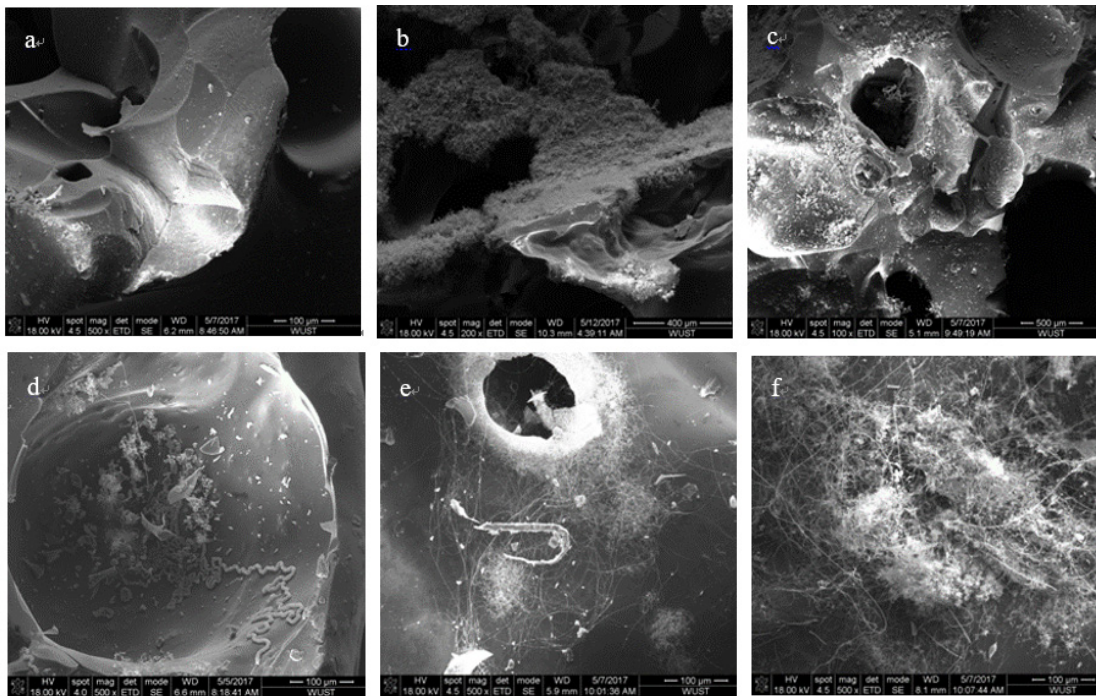


Figure 4. SEM images of a Ni- $x$ PF sample carbonized at 1000 °C for 3 h: (a)  $x = 0$ , (b)  $x = 0.01$ , (c)  $x = 0.02$ , (d)  $x = 0.03$  and (e)  $x = 0.04$ .

Figure 4(a) shows that ordinary phenolic resin pyrolysis charcoal is a disordered glassy carbon with no carbon nanotube structure on the pyrolysis carbon surface or at the fault. From the figure 4(b-f), it can be seen that different concentrations of the Ni catalyst can carbonize the modified phenolic resin to produce a large amount of carbon nanotubes. With the increase of nickel content, the carbon nanotubes showed a gradually increasing trend and the structure was more obvious. Because with the increase of the nickel content of the catalyst, the content of C-Ni solid solution was increased to a large extent. The more carbon nanotubes formed with the single nickel as the node, and the more obvious the structure is, the fewer defects are.

Comparing figure 5(a-c), it can be found that the produced carbon nanotubes have more defects and the yield is less at 1100°C. It can be considered that when the heating rate is low, the rate of formation of nickel ions by nickel ions is low. Thus carbon compounds form gaseous elements and the rate of formation of carbon nuclei on the nickel substrate is also low. When the heating rate increases, the rate of formation of nickel ions by nickel ions is accelerated. And carbon compounds form the gas elements and a large number of carbon nuclei on the nickel substrate, which increases the content of C-Ni solid solutions. It can produce less defective carbon nanotubes with simple nickel as a node. It can also increase the utilization efficiency of the catalyst. However, when the heating rate reaches 20° C/min, the reaction time is too short, and the amount of carbon compounds that form carbon nuclei on the nickel substrate is small, and C-Ni solid.



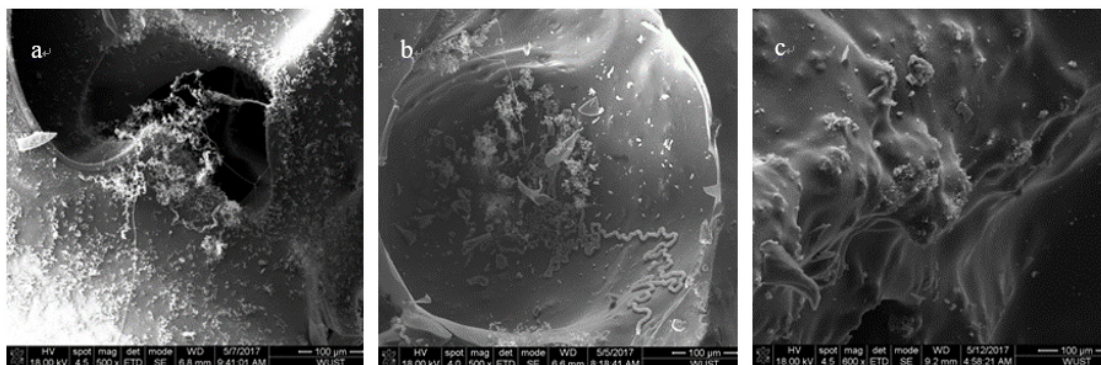


Figure 5. SEM images of Ni<sub>0.02</sub>-PF samples at different heating rates at 1100°C: (a) 5°C/min, (b) 10°C/min and (c) 20°C/min

#### 4. Conclusion

**Modified Thermoplastic Phenolic Resin Optimal Conditions:** The optimum conditions of the modified thermoplastic phenolic resin: the molar ratio of formaldehyde to phenol is 0.85, and oxalic acid accounts for 2% of the mass of phenol. The reaction temperature is 100° C. The reaction time is 2 h. The molar ratio of iminodiacetic acid to phenol is 0.03. The molar ratio of nickel sulfate to phenol is 0.04. The chelating temperature is 60° C, and the chelating time is 40 min. Nickel ions are grafted into the phenolic resin by the way of coordinative bonds. The atoms participating in the coordination are oxygen in the phenolic hydroxyl group, nitrogen in the imino group, carboxylic acid oxygen in the iminodiacetic acid, and oxygen in the free water.

The molar ratio of nickel sulfate to phenol is 4%, the carbonization temperature is 1100°C, and the heating rate is 10°C/min. This is the best process condition for preparing carbon nanotubes.

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