



The effect of zirconium incorporation on the thermal stability and carbonized product of phenol–formaldehyde resin



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ABSTRACT

A kind of zirconium modified phenolic resin (Zr-PF) was prepared by using phenol, paraformaldehyde, $ZrOCl_2 \cdot 8H_2O$, acetylacetone, ethanol and H_2O_2 as raw materials. The structure of the Zr-PF was characterized by Fourier transform infrared (FT-IR) spectra and solution ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra. The viscosity and thermal degradation behaviors of the Zr-PF were studied by rotary viscometer and thermogravimetric analyzer–differential scanning calorimetry (TG-DSC), respectively. The carbonized products of ordinary phenolic resin (PF) and Zr-PF were further investigated by X-ray diffraction (XRD), laser Raman spectroscopy (Raman) and scanning electron microscopy (SEM). Results show that new chemical bonds are formed through coordination reactions between zirconium atoms in Zr–OH and oxygen atoms in the acetylacetone and hydroxymethyl phenols. Viscosity of the Zr-PF is higher than that of PF during 30–80 °C. Compared with PF, thermal stability of the Zr-PF is obviously improved and its char yield is 55% at 1200 °C, 8% higher than that of PF. The d_{002} value of carbonized Zr-PF decreases from 0.3470 nm (carbonized PF) to 0.3329 nm and its crystallite height increases from 23.89 nm (carbonized PF) to 29.21 nm due to zirconium incorporation. In addition, the $ID/(ID + IG)$ value of carbonized Zr-PF decreases from 0.571 (carbonized PF) to 0.364 and the crystallite size of it increases from 29.90 nm (carbonized PF) to 44.79 nm. The results prove that the incorporation of zirconium exhibits obvious effects on promoting its graphite crystallite. What is more, the morphology of the carbonized Zr-PF changes from poor structure with many pore defects into dense and uniform matrix with uniformly dispersed ZrC particles.

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1. Introduction

Phenol–formaldehyde resin (PF) is still used as a precursor for the matrix of carbon/carbon composites due to its good mechanical properties and heat resistance after carbonization. In recent years, much efforts has been made to improve its mechanical properties and heat resistance by incorporating functional groups or other elements into polymer chain of phenolic resin such as boron, silicon, titanium and phosphorus etc. [1–5]. These modified resins are widely used in the process of polymer infiltration and pyrolysis technique to prepare refractory carbide modified carbon/carbon composites (C/C) in order to improve the ablation resistance of C/C by forming ceramic particles [6–8]. Zirconium tends to form Zr–O bond with a bond energy of 776 kJ mol⁻¹, which is much higher than that of C–C bond of 345 kJ mol⁻¹ [9]. Therefore, the thermal stability of phenolic resin would be improved after modified by

zirconium and it may also be an effective way to use it as an organic precursor to prepare zirconium modified carbon/carbon composites. Furthermore, it is found that zirconium can also improve the graphitization of disordered carbon materials [10]. Wang [11] tried to prepare zirconium modified phenolic resin (Zr-PF) by using phenol, paraformaldehyde, $ZrOCl_2 \cdot 8H_2O$ as raw materials, but the difficulties in controlling the reaction process and viscosity of the obtained product limited the further development of Zr-PF. While there are few reports about zirconium modified phenolic resin so far. Moreover, the effect of zirconium element on the properties of PF, especially on the pyrolysis and carbonization has not been further studied.

In the present work, phenol, paraformaldehyde, $ZrOCl_2 \cdot 8H_2O$, acetylacetone, ethanol and H_2O_2 were used as raw materials to introduce zirconium into phenolic resin through chemical reactions. The reaction process was easily controlled to avoid gelation and the product was kept in low viscosity. Structure of the Zr-PF was characterized by Fourier transform infrared (FT-IR) spectra and solution ^{13}C nuclear magnetic resonance (^{13}C -NMR) spectra. Viscosity and thermal degradation behavior of the resin were

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analyzed by rotary viscometer and thermogravimetric analyzer–differential scanning calorimetry (TG–DSC). In addition, carbonized products of the Zr-PF and PF were also analyzed by X-ray diffraction (XRD), laser Raman spectroscopy (Raman) and scanning electron microscopy (SEM), respectively.

2. Experimental

2.1. Materials

Phenol and paraformaldehyde (PA) were obtained from Tianjin Fuchen Chemical Reagent Co., Ltd.; zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), ethanol, acetylacetone were obtained from Tianjin Fengyue Chemical Reagent Co., Ltd.; H_2O_2 (concentration: 30%) and NaOH were obtained from Tianjin Fuyu Chemical Reagent Company. All reagents were used as received.

2.2. Synthesis of zirconium modified phenolic resin

The zirconium modified phenolic resin (Zr-PF) was synthesized as presented in Fig. 1. Phenol, paraformaldehyde and NaOH were added into a three-necked flask placed in a heated water bath equipped with a condenser and a mechanical stirrer. The mixture was stirred to be a homogeneous solution, and reacted at 70–75 °C for 1–1.5 h. Then an inorganic hybrid solution which was prepared by dissolving $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, Hacac and H_2O_2 in ethanol was added into the solution and reacted at 90 °C for 1–2 h. A red–brown semi-liquid product Zr-PF was obtained by removing residual solvent. And the phenolic resin with zirconium content from 0 to 20% would be synthesized by changing $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ inorganic hybrid solution molarity. In the following research, phenolic resin with zirconium content of 10% was mainly studied as representative sample. The ordinary PF was also prepared with the same process for comparison.

2.3. Purification of zirconium modified phenolic resin

To eliminate the effect of residual reactants, especially the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ inorganic hybrid solution, on the test results of obtained zirconium modified phenolic resin (Zr-PF), Zr-PF was purified by the following steps. Firstly, the Zr-PF was added into dilute sodium hydroxide solution, and then washed the resulting precipitate with deionized water for 3–4 times. Finally, the precipitate was removed by sedimentation in the centrifuge using deionized water as a solvent. After having repeated these steps for three times, the final product was dried in vacuum oven for 3 h at 65 °C.

Thus the purified Zr-PF without curing was used as the sample in the following characterization and heat-treatment.

2.4. Characterization

The structure of the Zr-PF was characterized (coating method) by FT-IR (Vector-22, Bruker, Germany) and solution ^{13}C -NMR (Mercury Plus Varian-300, Varian, USA) using DMSO as a solvent. Viscosity of the resin was analyzed by rotary viscometer (NDJ-5S, Changji, China). Thermal degradation behavior of the resin was analyzed by means of TG-DSC (STA429CD/3/7, Netzsch, Germany) at a heating rate of 5 °C min^{-1} from 30 °C to 1200 °C in nitrogen atmosphere. To further investigate the effect of zirconium on microstructure of carbonized PF, carbonized products of the PF and Zr-PF were studied by Raman (Renishaw, United Kingdom) and XRD (X'Pert Pro MPD, PANalytical, Netherlands). The heat treatment of both samples was carried out in a graphite crucible using a high-temperature graphite resistance furnace (ZGSS-400, Jinzhou, China) at temperature of 2000 °C for 2 h in argon gas with a heating rate of 10 °C min^{-1} , then cooled to room temperature slowly. Morphology of the carbonized products was analyzed by SEM (Amray 1000B, USA).

3. Results and discussion

3.1. Chemical structure of zirconium modified phenolic resin (Zr-PF)

A comparison of FT-IR spectra of PF and Zr-PF is shown in Fig. 2. The characteristic absorption peaks of the Zr-PF are shown in Table 1. The peaks at 1597 cm^{-1} and 1506 cm^{-1} are due to C=C stretching of benzene rings and peaks at 888 cm^{-1} , 821 cm^{-1} , 757 cm^{-1} could be assigned to C–H flexural vibration of benzene rings. All of these bands are characteristic absorption bands of PF. While compared with the curve of PF, an increase in the band at 1450 cm^{-1} (stretching vibration of C=O) indicates that coordination compound was obtained by coordination reaction between $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ hydrolyzates (Zr–OH) and acetylacetone [12]. Moreover, the band at 560 cm^{-1} is assigned to be the vibration of Zr–O [13]. As the effect of residual reactants (especially the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ inorganic hybrid solution) has been eliminated, the appearance of Zr–O absorption peak is believed to be caused by the zirconium introduced into the reaction product. Based on the analysis above, it can be concluded that zirconium has been incorporated into the reaction product and exists in the form of Zr–O bond.

A comparison of ^{13}C NMR spectra of PF and Zr-PF is shown in Fig. 3. The major chemical shifts the PF and Zr-PF are summarized in Table 2. Compared with the ^{13}C NMR spectra of PF, chemical

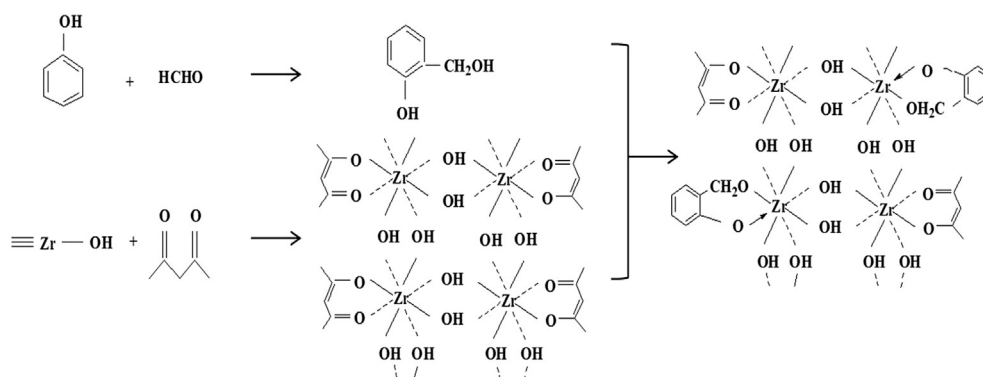


Fig. 1. Reaction scheme for preparation of the zirconium modified phenolic resin.

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