

# The effect of titanium incorporation on the thermal stability of phenol-formaldehyde resin and its carbonization microstructure

Yan Zhang\*, Shihong Shen, Yujian Liu

Key Laboratory for Specially Functional Polymers and Related Technology of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Mei-Long Road 130, 200237 Shanghai, China

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## ABSTRACT

A new titanium modified phenolic resin (Ti–PF) was prepared by using tetraisopropyl titanate, phenol and formaldehyde with mild and friend reaction condition. The structure of the modified resin was demonstrated by means of FT-IR spectra. The titanium modified resin is soluble only in a few solvents such as DMF, DMAc, DMSO, but exhibits poor solubility in most universal solvents. The thermal degradation behavior of the Ti–PF was studied by thermal gravimetric (TG) method. Compared with the unmodified resin (PF), the temperature at the maximum decomposing rate of the Ti–PF increases by 43 °C and its charring yield enhances by 11 percent. The carbonized products of PF (C–PF) and Ti–PF (C–Ti–PF) were further investigated by X-ray diffraction and Roman spectroscopy, respectively. The analysis indicates that the incorporation of titanium into carbon lattice results in an increase of crystallite height and decrease of interlayer spacing. Titanium modified PF becomes much more ordered with a  $d_{002}$  of 0.3572 nm as compared to that of 3.7811 nm for C–PF. And the crystal size of C–Ti–PF increases to 4.37 nm, 2.13 nm larger than that of C–PF. In addition, the  $I_D/I_G$  value of C–Ti–PF decreases from 2.85 (C–PF) to 2.62. The results prove that the incorporation of titanium exhibited obvious effects on improving thermal stability of the phenolic resin and on promoting its graphite crystallite.

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## 1. Introduction

Phenol-formaldehyde resin (PF) is an excellent thermosetting resin with good mechanical properties and heat resistance, and it has been used in preparing fiber glass reinforced laminate, molding compounds, thermal insulation materials, coating, and adhesive. However, the rapid growth of PF applications has promoted extensive research to improve its heat resistance and mechanical properties, especially high-temperature ablation and charring yield. One approach is related to the incorporation of various elements or functional groups into the backbone of phenolic resin, such as boron, phosphorus, silicon, molybdenum, zirconium compounds and phenyl-phenol etc [1–7]. Titanium tends to form covalent bond with oxygen and the bond energy of Ti–O is 662 kJ mol<sup>-1</sup>, which is much higher than that of C–C bond (345 kJ mol<sup>-1</sup>). So the thermal stability of phenolic resin can be greatly improved after modified by titanium. In addition, it is found that titanium also has good catalytic properties for graphitization of the disordered carbon materials [8–11]. Tugtepe and Ozgumus [12] tried to prepare titanium modified phenolic resin (Ti–PF) by using

titanium tetrachloride during early twenties century, but the rigorous reaction condition and the release of hydrogen chloride gas limited the further development of Ti–PF. So the research on synthesis and applications of titanium modified phenolic resin is very little reported, to our best knowledge. Moreover, the effect the titanium element on the property of the phenolic resin, especially thermal stability and carbonation mechanism has not been further investigated. In the present work, tetraisopropyl titanate was selected for synthesizing Ti–PF. No poisonous and corrosive gas was released in the preparation, and the reaction condition was mild. The structure of the Ti–PF was characterized by FT-IR. In addition, the thermal decomposition property of the modified resin was followed by means of TGA. And the carbonized products of the titanium modified resin and ordinary phenolic resin were also analyzed by X-ray diffraction and Roman spectroscopy.

## 2. Experimental

### 2.1. Materials

Tetraisopropyl titanate (AR) was obtained from TCI Company, formaldehyde (AR), phenol (AR) were obtained from Shanghai Ling Feng Chemical Reagent Co., Ltd. All reagents were used as received.

\* Corresponding author. Tel./fax: +86 21 64252659.

E-mail address: [yzhang@ecust.edu.cn](mailto:yzhang@ecust.edu.cn) (Y. Zhang).

## 2.2. Synthesis titanium modified phenolic resin

The titanium modified phenolic resin (Ti–PF) was synthesized as presented in Fig. 1. Phenol and tetraisopropyl titanate were added into a three-necked flask equipped with a mechanical stirrer, a thermometer and a condenser. The mixture was stirred to form a homogeneous phase, and reaction continued at refluxing temperature for 2–3 h. Then formaldehyde and catalyst were added to the mixture. The reaction temperature was increased to 90 °C, and reaction lasted for 1–2 h. After removing water through vacuum distillation, a red solid product, Ti–PF was obtained. Changing molar ratio of phenol and tetraisopropyl titanate can yield phenolic resin with titanium content from 1% to 10%. TG analysis shows that Ti–PF with 1%(wt%) titanium content has highest charring yield, so in the following research the Ti–PF is just referred to this type of resin. The ordinary phenol-formaldehyde resin (PF) was prepared with conventional method [13] for comparison.

## 2.3. Samples characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5700 spectrometer. The TG analysis of 10 mg sample, which was cured at 165 °C for 4 h, was performed according to the thermal-analysis instruction (NETZSCH STA 449C) at a constant heating rate of 10 °C min<sup>-1</sup> in nitrogen atmosphere from 40 °C to 850 °C. The degree of carbonization of the samples, the matrix microstructure and the properties of the carbonized PF (C–PF) and Ti–PF (C–Ti–PF) were characterized by X-ray diffraction (XRD) and Raman spectroscopy. Samples for XRD analysis were mounted on an agate mortar with 0.2 mm depth, and patterns were recorded on a Rigaku D/max-2550VB+/PC system, using Cu K<sub>α</sub> radiation (λ = 0.154 nm, 40 kV, 100 mA) over the range of 3°–80° (2θ) at room temperature. The Raman spectra were collected using a Renishaw inVia Reflex system at an excitation wave length of 514.5 nm.

## 3. Results and discussion

### 3.1. IR analysis of titanium-modified phenolic resin (Ti–PF)

A comparison of the IR spectra of ordinary phenolic resin (PF) and titanium-modified phenolic resin (Ti–PF) is shown in Fig. 2. The characteristic absorption peaks of titanium-phenolic resin are shown in Table 1. The characteristic peaks at 1611 cm<sup>-1</sup> and 1594 cm<sup>-1</sup> correspond carbon–carbon double bonds(C=C) of benzen rings and peaks at 887 cm<sup>-1</sup>, 825 cm<sup>-1</sup>, 757 cm<sup>-1</sup> correspond to the C–H flexural of benzene rings, all of which are characteristic absorption bonds of phenolic resin. Compared with the unmodified phenolic resin (curve a), a new absorption band at 645 cm<sup>-1</sup> corresponds to the Ti–O bond appears. It demonstrates that the titanium element was introduced into the backbone of the phenolic resin.

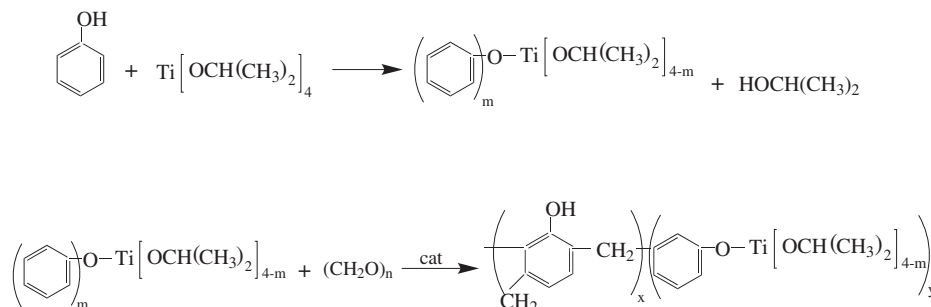


Fig. 1. Reaction scheme for preparation of the titanium modified phenolic resin.

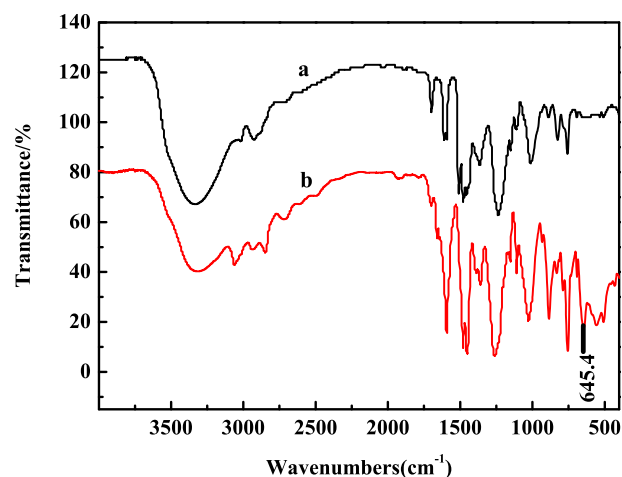


Fig. 2. FT-IR spectra of ordinary phenolic resin and titanium-modified phenolic resin, a) ordinary phenolic resin, b) titanium modified phenolic resin.

### 3.2. Solubility of titanium modified phenolic resin (Ti–PF)

It is important to choose a suitable solvent for the matrix resin in preparing filament prepreg. The solubility of Ti–PF was evaluated in various solvents, and the results are listed in Table 2. Ti–PF exhibits good solubility in strong polar solvents, such as DMF, DMAc, DMSO, but shows poor solubility in some universal solvents like ethanol, acetone, toluene, tetrahydrofuran, etc. This may attribute to the incorporation of bulk titanium oxygen bond in the Ti–PF molecular structure, which tends to be steric hindrance of main chain, decrease the conformational entropy of molecule, and increase the free energy of solution. At the same time, less hydroxyl groups of the system will result in decrease of the polar of the modified resin, which also make the solubility difficult. The poor solubility of Ti–PF in universal solvents may restrict its application in some fields.

### 3.3. Thermal stability of Ti–PF

The thermal stability of PF and Ti–PF in nitrogen atmosphere was investigated by TGA. The TG and the derivative thermal gravimetric (DTG) profiles are shown in Fig. 3. The pyrolysis processes of cured PF and Ti–PF are similarly, in both of which three major reaction regions exist. In the first region, there is mainly evolution of water and unreacted oligomers [14]. The initial decomposition temperature of PF and Ti–PF are both about 300 °C. Up to 500 °C, the polymer network remains essentially unaffected, whereas above 500 °C dramatic changes can be noticed, leading to the collapse of the network and formation of polyaromatic domains [14–16].

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