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

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A B S T R A C T

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.

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^{-1}, which is much higher than that of C—C bond (345 kJ mol^{-1}). 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.

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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^{-1} 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$_\alpha$ radiation ($\lambda = 0.154$ 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^{-1} and 1594 cm^{-1} correspond carbon–carbon double bonds(C═C) of benzen rings and peaks at 887 cm^{-1}, 825 cm^{-1}, 757 cm^{-1} correspond to the C–H flextural 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^{-1} corresponds to the Ti–O bond appears. It domonstrates that the titanium element was introduced into the backbone of the phenolic resin.

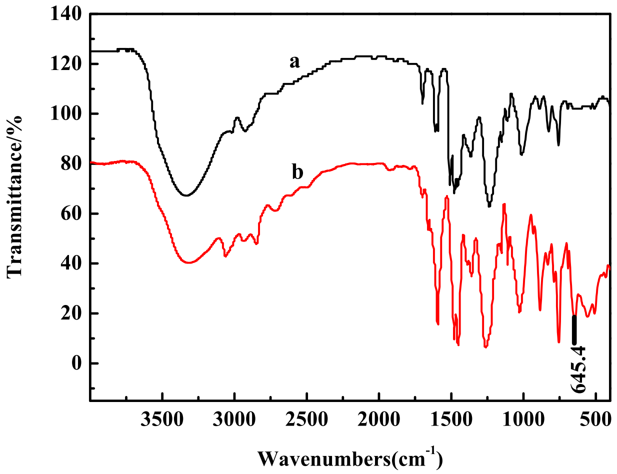

Fig. 2. FT-IR spectra of ordinary phenolic resin and titanium-modified phenolic resin, a) ordinary phenolic resin, b) titanium modified phenolic resin.

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].

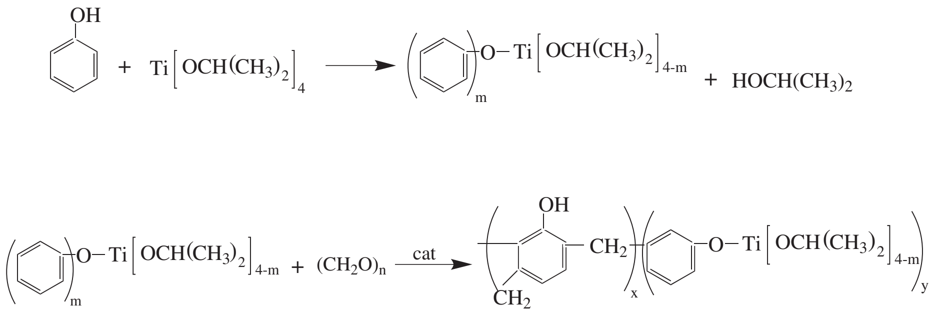

Fig. 1. Reaction scheme for preparation of the titanium modified phenolic resin.

Table 1
Characteristic absorption peak of titanium–phenolic resin.

The peak of absorption band (cm^{-1})	Chemical bond
3318	–OH stretching of phenolic ring
1611, 1509, 1594, 1487	C=C stretching of phenolic ring
1455, 1361	Scissoring vibration of $-CH_2-$
1237	Stretching vibration of C–O
1150, 1106	Stretching vibration of CH_2-O-CH_2
1038	C–O stretching of hydroxymethyl
887	C–H flexural of phenolic ring meta position
825	C–H flexural of phenolic ring para positon
757	C–H flexural of phenolic ring ortho position
645	Vibration of Ti–O

Table 2
The solubility of Ti–PF in various solvents.

Solvent	Solubility	Solvent	Solubility
Methanol	−	Tetrahydrofuran (THF)	−
Ethanol	−	Toluene	−
Butanol	−	Xylene	−
Isopropanol	−	Dioxane	−
Acetone	−	Dichloromethane	+
Butone	−	Ethyl acetate	−
N,N-dimethylformamide (DMF)	+	Tetrachloromethane	−
N,N-dimethylacetamide (DMAc)	+	n-hexane	−
Dimethyl sulfoxid (DMSO)	+	Thionyl chloride	+
Chloropropylene oxide	+	n-pentane	−

+ Soluble; − insoluble.

Although only 1 percent titanium is introduced into the backbone of the phenolic resin, the temperature at the maximum decomposing rate of the Ti–PF is 554 °C, an increase of 43 °C compare to that of the unmodified phenolic resin. Moreover, the char yield of Ti–PF at 850 °C is 73.3%, which is also eleven percent higher than the latter. It indicates that the high temperature resistance of the phenolic resin is significantly improved owing to the introduction of titanium element. This can be attributed to the higher bond energy of Ti–O, which is 662 kJ mol^{-1}, much higher than C–C bond (345 kJ mol^{-1}). On the other hand, in the titanium-modified phenolic resin, a hyperbranched structure will be formed during curing reaction, which also tends to enhance its char yield. Moreover, titanium may further work on carbonization process of the phenolic resin.

Fig. 4 shows the TG curve of cured titanium-modified phenolic resin in air atmosphere. As shown in the X-ray diffraction profile of the carbonized Ti–PF heating treatment at 800 °C in air for 10 h (Fig. 5), phases consist of anatase and rutile are apparent. All peak lattice parameters correspond to TiO_2 phase. So titanium content of the modified resin can be calculated from the residue (TiO_2) mass (2.0%) according to Fig. 4. Titanium element introduced into the resin is 1.2% (wt%), consistent with the experiment data, 1.0%.

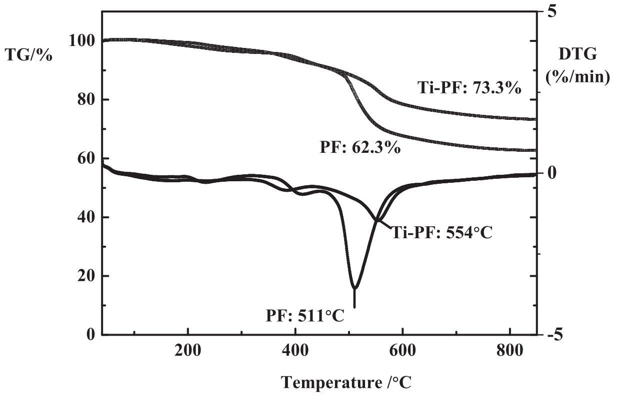

Fig. 3. TG and DTG curves of ordinary PF and Ti–PF in nitrogen.

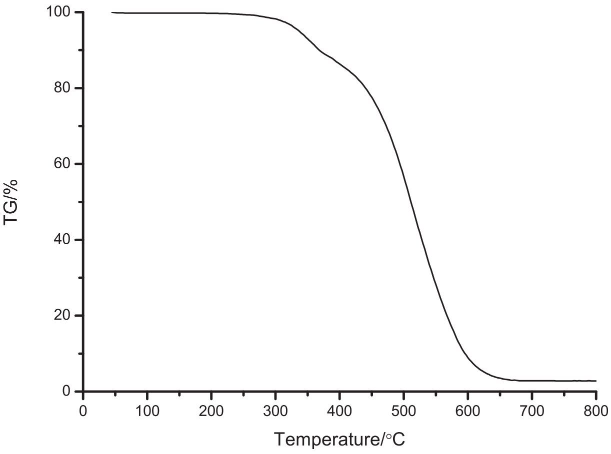

Fig. 4. TG curve of Ti–PF in air.

3.4. Microstructure analysis of carbonized Ti–PF

In order to further investigate the effect of titanium on the carbonization of the phenolic resin, carbonized products of the Ti–PF and PF were study by Raman and XRD. All samples were carbonized from room temperature to 950 °C at a heating rate of 10 °C min^{-1}, and keeping at 950 °C for 2 h under 0.5 ml min^{-1} nitrogen gas, then slowly cooled (5 °C min^{-1}) to room temperature, respectively. The obtained carbonized Ti–PF samples feature special metallic luster and higher hardness than that of PF.

The Raman spectrum of carbon contains valuable information about the atomic level microstructure [17]. Carbons show mainly two Raman bands, 1580 cm^{-1} and 1360 cm^{-1}. The former, which is referred as the G-mode, corresponds to the E_{2g} mode of graphite, and is assigned to the “in-plane” displacement of the carbons strongly coupled in the hexagonal sheets. The latter, which is absent in the single crystal graphite, corresponds to the defect-induced Raman band called the D-mode [17]. The relationship between the D band and the G band intensities should be proportional to the degree of structural order with respect to the graphite structure. This relationship has been largely used in the literature in different forms, such as I_D/I_G and $I_D/(I_D + I_G)$ [18]. The I_D/I_G and $I_D/(I_D + I_G)$

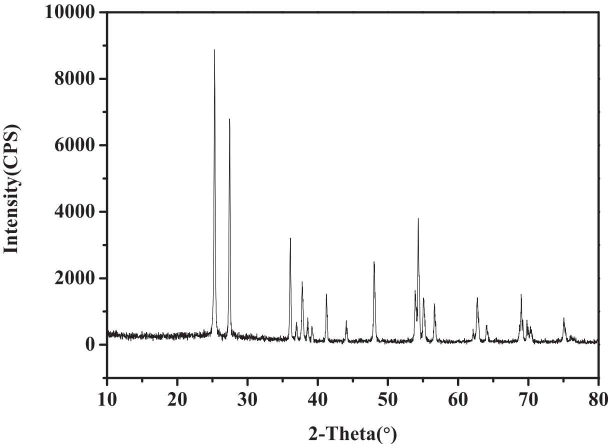

Fig. 5. XRD pattern of sample of carbonized Ti–PF at 800 °C heating treatment for 10hr in air.

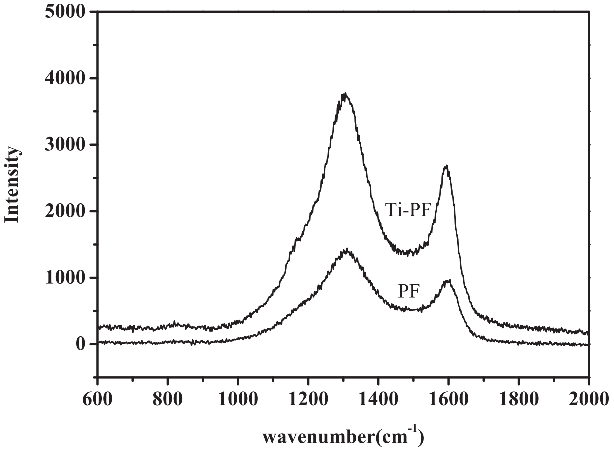

Fig. 6. Raman spectra of carbonized PF and carbonized Ti–PF.

Table 3
Raman spectra parameters for carbonized PF and carbonized Ti–PF.

Sample	I_D/I_G	$I_D/(I_D + I_G)$	L_a (nm)
PF	2.85	0.74	1.54
Ti–PF	2.62	0.72	1.68

intensity ratios reflect the disorder. And the microcrystalline planar size (L_a), which corresponds to the in-plane dimension of the single microcrystalline domain in carbonized products, can be determined from the integrated intensity ratio I_D/I_G as follows:

$$L_a = 44[I_D/I_G]^{-1}$$

The Raman spectra measured for the C–PF and Ti–PF are shown in Fig. 6. And data analysis is shown in Table 3. Compared with that of C–PF, the value I_D/I_G of C–Ti–PF decreased from 2.85 to 2.62. The crystal size La of C–Ti–PF is 1.68, a little bigger than that of C–PF. The changes in the Raman spectra of PF demonstrate that the rearrangement of crystalline structure leads to an increase of graphite structure and a decrease of disordered structure after introducing titanium into the backbond of the resin. Titanium elements may be incorporated within the graphene cyclic systems, so it can be considered as catalysts for promoting the increase of the crystal size [8–11]. However, the value of $I_D/(I_D + I_G)$ for both samples was greater than 50%. This means that two carbonized resins are the more disordered materials. The temperature of 950 °C is still too low for phenolic resin complete graphitization.

The X-ray powder diffraction patterns of both samples carbonized at 950 °C are shown in Fig. 7. Two broad maxima, corresponding to (002) and (10) reflections of a turbostratic carbon structure, are observed at 2θ angles of about 24° and 44°, respectively. Although diffraction patterns of C–Ti–PF are similar to that of C–PF, obvious difference can be seen. Some new minor peaks appear at $2\theta = 37.7°$, 47.7°, 62.0° in C–Ti–PF curve, corresponding to (111), (200) and (220) reflection of lattice plane for Ti–PF, which may be assigned to TiC, respectively. It indicates that TiC should be formed during the carbonization of the phenolic resin. TiC, with high melting points, hardness, stiffness and combined with good corrosion and oxidation resistance, also makes itself an ideal candidate as protective coating materials under extremely harsh and corrosive environments [19]. It illustrates that with only incorporation of 1% titanium into the backbone of the resin, the thermal stability and charring yield of PF can be greatly improved. In addition, the other minor peaks ($2\theta = 25.2$, 53.8°) mean formation TiO_2 phases in the products. The oxygen atom may come from the impurity of the atmosphere and the resin itself.

Despite the non-graphitizable character of both carbonized products, the crystallinity was greatly improved due to the presence of titanium. Titanium incorporation has a little effect to the parameters of diffraction peak and crystallite sizes. Table 4 lists crystal parameters of the C–PF and C–Ti–PF. The basal spacing d_{002} for the carbides is calculated according to the Bragg formula $\lambda = 2d_{002}\sin\theta$. The crystallite size ($L_a$), the stacking size of carbon basal planes (L_c crystal thickness) can be calculated by the following expressions [20], respectively:

$$L_a = 9.5/(d_{002} - 3.354);$$

$$L_c = K\lambda/B\cos\theta;$$

where $\lambda = 0.154$ nm, K is the apparatus constant (=1.0), and B is the half value width in radians of the X-ray diffraction intensity (I) vs. 2θ curve.

It can be clearly noted that the 002 diffraction peak of C–Ti–PF, at 2θ about 24°, has the tendency to shift to the larger angle direction compared with that of C–PF. The d_{002} values of two carbonized products are both higher than 0.3500 nm, exhibiting glassy carbon character [21,22]. However, the d_{002} value in the C–Ti–PF sample

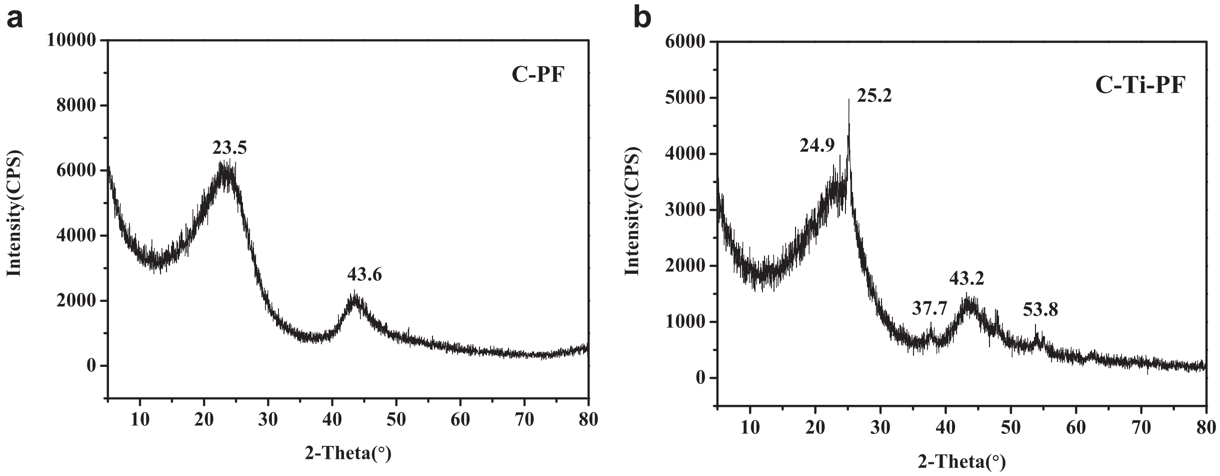

Fig. 7. XRD patterns of C–PF and C–Ti–PF samples a) C–PF, b) C–Ti–PF.

Table 4
Parameters of 002 and 10 diffraction peaks for carbonized PF and Ti–PF.

Sample	$2\theta(002)$	$2\theta(100)$	d_{002}/nm	L_a/nm	L_c/nm
PF	23.5	43.6	0.3781	2.24	0.77
Ti–PF	24.9	43.2	0.3572	4.37	1.01

decreases (0.3572 nm) compared to that of the C–PF sample (0.37811 nm), suggesting the presence of titanium in a substitutional position. And the order degree of the carbonized product is improved, too.

Moreover, the L_c and L_a values for C–Ti–PF are both higher than that of C–PF. This indicates that the growth of crystallite is enhanced by the existence of titanium. The incorporation of titanium into carbon lattice results in an increase of crystallite height and decrease of interlayer spacing. The results of Raman spectroscopy analysis conform to those of XRD.

4. Conclusions

A novel titanium modified phenolic resin was synthesized and its structure was demonstrated by means of IR spectra. Ti–PF is soluble only in a few solvents such as DMF, DMAc, DMSO, but exhibits poor solubility in universal solvents, which may restrict its usage in some fields. The temperature at the maximum decomposing rate of the Ti–PF is 554 °C, 43 °C higher than that of the unmodified ones. Moreover, the charring yield of Ti–PF is 73.3%, 11.0 percent higher than that of PF. The structure of carbonized PF and Ti–PF were studied by using X-ray diffraction and Roman spectroscopy. Titanium incorporation can not only improved thermal stability of the phenolic resin, but also can affect microstructure of the carbonized resins. The I_D/I_G value of C–Ti–PF decreases from 2.85 (C–PF) to 2.62. The degree of graphitization of the phenolic resin is improved owing to titanium incorporation. And the crystal size of C–Ti–PF increases from 2.24 nm (C–PF) to 4.37 nm. The incorporation of titanium into the carbon lattice results in an increase of crystallite height and decrease of interlayer spacing.

Acknowledgments

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