

Structure and Surface Elemental State Analysis of Polyimide Resin Film after Carbonization and Graphitization

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ABSTRACT: The carbon materials prepared from polyimide (PI) resin film were investigated by TG-DTG, X-ray powder diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analysis. TG-DTG study revealed that the weight loss of PI resin film during carbonization occurred in three stages, and the most serious changes occurred at 605.5°C. XRD results indicated that a disorder structure occurred after the carbonization at 600°C and graphite crystallite appeared gradually with increasing the temperature. And PI resin film still presented some characteristics of nongraphitizing carbon, after graphitizing at

2600°C. XPS analysis identified that pyrrole type nitrogen was a main component of surface nitrogen atoms after carbonization. When the temperature reached 2600°C, nitrogen atoms disappeared totally; the reason why oxygen atoms still existed in the material at so high temperature was our subject of interesting matter in the later study. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1852–1856, 2008

Key words: polyimide film; resin; TGA; structure; surface elements state

INTRODUCTION

Polyimide film with special molecule structure was an attractive material as precursor for carbon film, as well as thermo resistant polymers, from fundamental and practical points of view. In the former studies, people focused on its high degree graphitization treated under special conditions.^{1–3} Graphitization behavior of aromatic polyimide “Kapton” was studied by transmission electron microscopy, X-ray diffraction, and transport property measurements.^{4–6} From these experiments, three factors for getting graphitizing carbon films were pointed out: (1) flat and rigid starting molecules; (2) high degree of preferred orientation of the molecules along the film surface; (3) less disturbance of the molecular orientation during departure of noncarbon atoms. Here, it should be emphasized the thickness impacted the degree of orientation: the thinner the better.⁷

By now, there were few systemic studies about the structure and surface elemental state changes of polyimide (PI) resin film with temperature. We choose PI resin film with a thickness of 75 μm as precursor,

and for the first time heat-treated it without pressure. In this work, the weight changes during carbonization were analyzed by TG-DTG, and the structure changes of PI resin film with temperature were studied by X-ray powder diffraction (XRD). The surface elements composition at different temperatures was analyzed by X-ray photoelectron spectroscopy (XPS), and the chemical bonding state of atoms in hexagonal carbon layers was also discussed from a theoretical standpoint.

EXPERIMENTAL

Preparation of samples

The rectangular specimens with area of $3 \times 10 \text{ cm}^2$ were cut from a large sheet of PI resin film supplied by Insulation materials factory in Tianjin. And these sheets were put in a steel boat, and then carbonized in a carbonized furnace under high-purity N_2 gas. For carbonization, heat treatment temperatures for the residence time of 1 h were selected at 600, 800, 1000°C with a heating rate of 2°C/min. Further, the carbonized films up to 1000°C were heat-treated at 2600°C, and then the five samples were crashed into powder. We signed these samples as PI600, PI800, PI1000, PI2600, respectively.

Thermogravimetric analysis

A computer-controlled thermogravimetric analyzer (TA-50, Japan Island Company) was used to study

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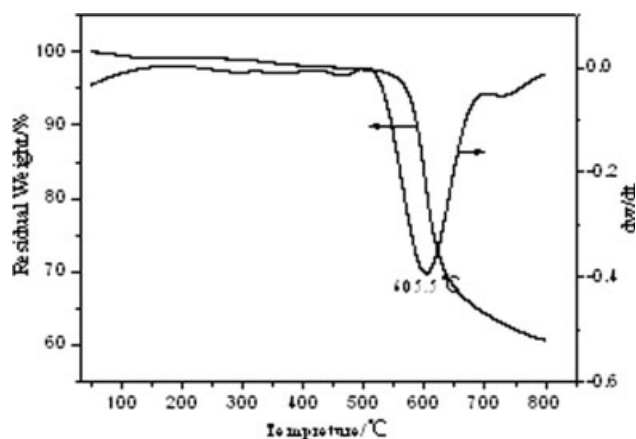


Figure 1 The TGA and DTG curves of PI resin film.

the weight change during heating process. The sample was heated from room temperature to target temperature under N_2 atmosphere at the heating rate of $10^\circ C/min$.

XRD analysis

The X-ray diffraction analysis was conducted by using a XRD (D/Max2500, Rigaku) equipment with $CuK\alpha$ X-rays ($\lambda = 0.154056$ nm) and Ni filter from 10° to 100° (2θ) with the step of 0.02° .

XPS analysis

XPS measurements were carried out using PHI-1600 ESCA system (America PE company) with $AlK\alpha$ ($h\nu = 1486.6$ eV)/ $MgK\alpha$ ($h\nu = 1486.6$ eV) two-cathode target. The analysis area of sample was 0.8 mm², and the depth of sampling was 2–5 nm.

RESULTS AND DISCUSSION

TGA analysis

PI resin film changed obviously during pyrolysis: its color became bright black from transparent brown, and its texture became brittle. The TGA and DTG curves of PI resin film were shown in Figure 1. It indicated that a total weight loss of about 40% during pyrolysis in N_2 was observed. The weight loss during carbonization comprised three phases. The first was a slight weight loss before $530^\circ C$ corresponding to the removal of retained water, which also indicated the good heat resistance of PI resin film. And the weight decreased continuously from 530 to $700^\circ C$, especially at $605.5^\circ C$ because most chemical decomposition reactions of the material took place in this temperature. This step of weight loss being mostly due to the conversion of four carbonyl groups ($C=O$) in the imide part to ether CO or CO_2 .⁸

Above $700^\circ C$, weight loss began to decrease. That was because the volatilizing of CO and CO_2 tended to decrease, CH_4 and H_2 started to evolve above $605.5^\circ C$, and the total quantity of gas formed became smaller. The chemical rearrangement reactions and cyclizations took place, and a graphite-like structure was formed gradually in this phase. Until $800^\circ C$, the gas evolution was almost finished except H_2 . Above $850^\circ C$, N_2 started to evolve.⁵

XRD characterization

Figure 2 displayed the wide-angle XRD patterns of PI resin film-derived carbon. The characteristic peaks at $2\theta = 5.7^\circ$ and 14.6° in origin film indicated the order supramolecular structure. When the temperature of heat treatment reached to $600^\circ C$, a broad peak appeared at $2\theta = 20.9^\circ$, suggesting that the material structure began to transform to amorphism. There were two broad peaks around $2\theta = 23.5^\circ$ and 43.2° in the XRD spectrum of PI800, corresponding to the diffraction of (002) and (100), respectively. The (002) peak broaden slightly and the (100) peak grew

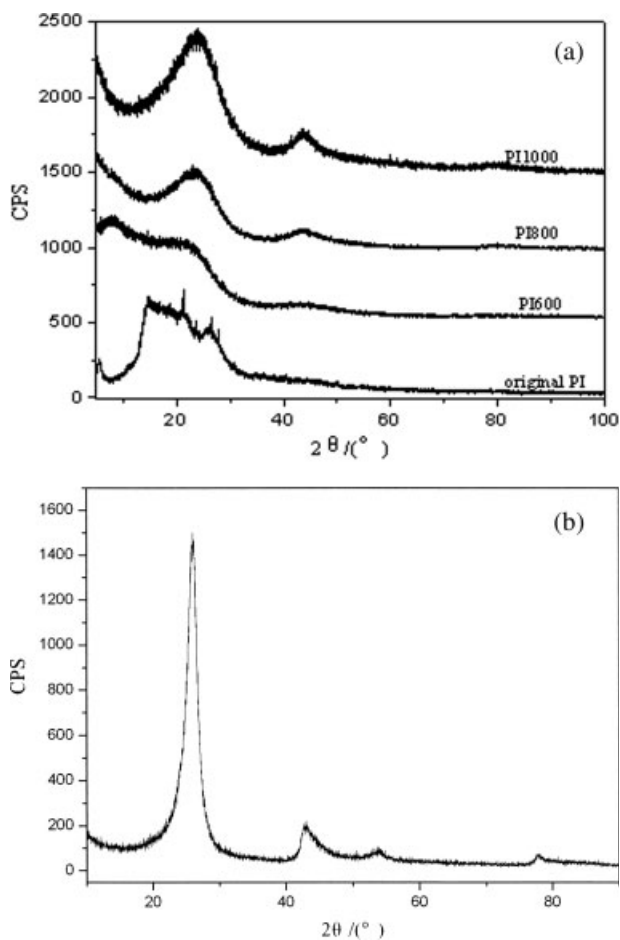


Figure 2 XRD curves of PI resin film-derived carbon (a) after carbonization (b) after graphitization.

TABLE I
Surface Elemental Composition According to XPS Analysis

Sample	C (%)	O (%)	N (%)
PI	75.9	20.3	3.8
PI600	85.4	11.2	3.4
PI800	86.1	11.4	2.5
PI1000	86.4	11.4	2.2
PI2600	93.4	6.6	0

to some extent with the carbonization temperature from 800 to 1000°C, suggesting that the three-dimensional arrangement in the carbonized PI resin film was gradually ordered.

After graphitization, the peak (002) became sharp and (004), (110) characteristic peaks also appeared at $2\theta = 53.7^\circ$ and 77.8° , respectively. The broad bottom of the (002) peak and the asymmetry of the (100) peak all showed that the sample had characteristics of hard carbon after graphitizing at 2600°C. Here, it should be emphasized the present (002) showed a far narrower peak than that of conventional turbostratic carbons; in other words, the sample had very thick crystallites, in spite of turbostratic structure.

We calculated the parameters d_{002} , Lc, and La for the (002) and (100) peaks using the Bragg and Scherer equations.⁹ It can be found that the value of d_{002} reached 0.3361 nm after graphitization, being close to the value of nature graphite (0.3354 nm). But

the value of Lc was only 3.7584 nm, which also indicated the characteristics of hard carbon.

Study by XPS

XPS experiments were performed on the five samples we prepared, so as to obtain information on elemental composition, nature, and an approximate evolution of the spatial distribution of the minority elements in the sample. The ratio of elements on the surface for all sample were summarized in Table I.

These values reflected that the surface carbon concentration rose gradually with temperature, the amount of oxygen concentration decreased rapidly to 11.2% from 20.3% after carbonized at 600°C, and then remained at this level (or rose somewhat) until 1000°C; whereas the significant changes of nitrogen began at 800°C, when the temperature reached 2600°C, no nitrogen atom was detected.

High-resolution fitted XPS spectra of C1s were shown in Figure 3. Deconvolution of the C1s spectra¹⁰ gave five peaks: that represent graphitic carbon (284.6 eV), carbon present in phenol, alcohol, ether or C=N groups (286.1–286.3 eV), carbonyl or quinone groups (287.3–287.6 eV), carboxyl or ester groups (288.4–288.9 eV), and carbon present in carbonate groups and/or adsorbed CO and CO₂ (290.4–290.8 eV).

The best fitting was invariably obtained for the samples with Gaussian lines, and the calculated per-

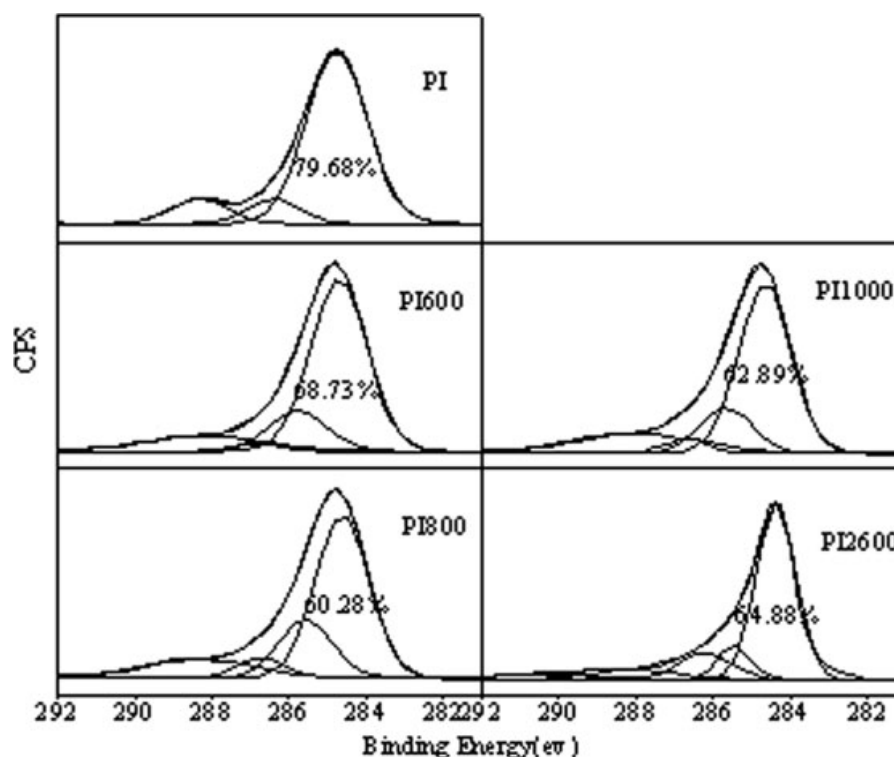


Figure 3 C1s X-ray photoelectron spectra of PI resin film carbonized at different temperatures.

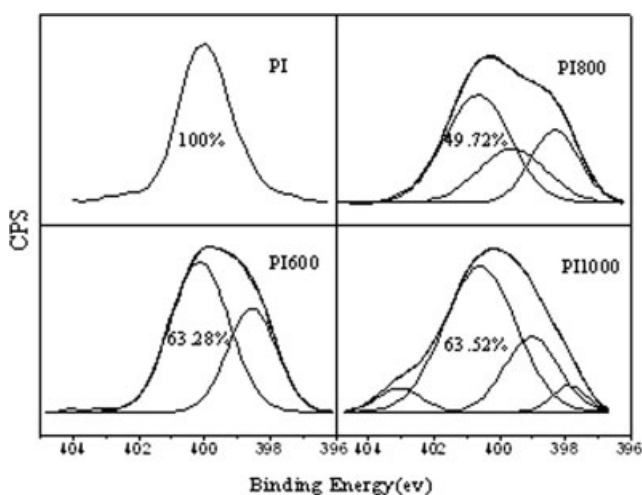


Figure 4 N1s X-ray photoelectron spectra of PI resin film carbonized at different temperatures.

centages of graphitic atoms were shown in Figure 3. The relative content of graphitic carbon decreased before 800°C and then rose with temperature. This showed the process origin resin with order supramolecular structure transformed to amorphous carbon with the volatilization of CO and CO₂, which is consistent with the TGA analysis. Until 1000°C, the percentages of graphitic atoms increased again corresponding to the form of graphite-like structure. The relative content of other carbon functional groups showed irregular changes, showing the complexity of structure changes during carbonization.

A complex XPS N1s spectrum of carbonaceous material had been usually fitted by four components¹¹ of binding energies: pyridinic nitrogen (N-6, 398.6 ± 0.3 eV), pyrrolic nitrogen (N-5, 400.5 ± 0.3 eV), quaternary nitrogen (N-Q, 401.3 ± 0.3 eV), and nitro nitrogen (N-X, 402–405 eV). Because no nitrogen atoms were detected at 2600°C, we just received

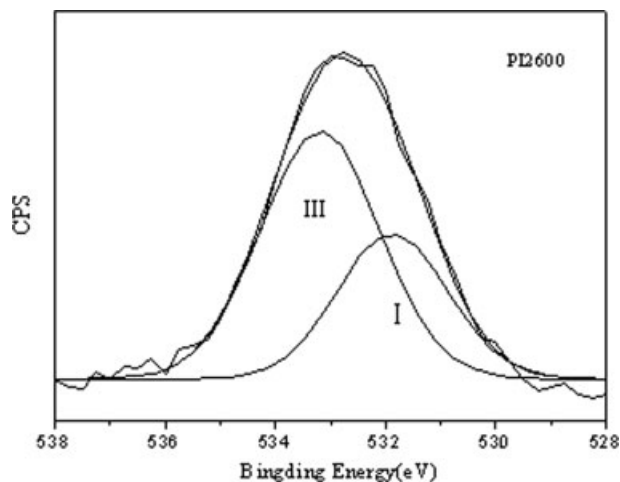


Figure 5 O1s X-ray photoelectron spectra of PI resin film carbonized at 2600°C.

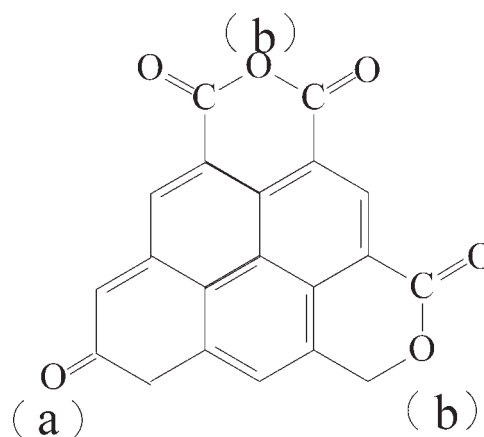


Figure 6 Binding mode of oxygen atoms in graphite layer after graphitization.

spectra of four samples. Figure 4 showed the fitting results of N1s spectra, and the calculated percentages of N-5. The spectrum of origin resin consisted of one N-5 peak present at 400.7 eV, corresponding to the molecular structure of PI resin film. At the conditions of high-temperature pyrolysis, N-5 was partly converted into N-6, according to our results. When the temperature reached 800°C, a new peak appeared at 399.6 eV,¹² and the percentages of N-5 decreased further.

After carbonized at 1000 °C, pyrrolic nitrogen became the main combining style again. A fourth peak was found at high binding energy at 403.05 eV, which may originate from some form of oxidized nitrogen. Besides, the new peak appearing at 800°C shifted to lower binding energy (399.0 eV).¹³ It also indicated the increasing of graphitic layer with the temperature.

The existence of oxygen atoms at 2600°C was an interesting phenomenon, the reason was still not clear. Similarly, the deconvolution of the O1s spectra yielded the five kind peaks.^{14,15} The O1s spectra of PI resin carbonized at 2600°C was shown in Figure 5. It appeared two peaks at 531.9 and 533.2 eV, respectively, according to the quinoid carbonyl (structure (a) in Fig. 6) and oxygen atoms in ester and anhydrides (structure (b) in Fig. 6), which was consistent with the fitting results of C1s.

CONCLUSION

This article studied the influence of carbonization and graphitization on the structure and surface element state of PI resin film. TG-DTG study revealed PI resin film was a thermo-resistant aromatic heterocyclic polymer. Its weight loss began at 530°C and decreased continuously with temperature. The most serious weight loss was at 605.5°C under high-purity

N₂ gas. Its color became bright black from transparent brown after heat treatment.

XRD results indicated that amorphous structure appeared after carbonization at 600°C with the appearing of the (002) characteristic peak. And three-dimensional arrangement of graphite layer was gradually ordered with increasing temperature from 600 to 1000°C. The broad bottom of the (002) peak and the asymmetry of the (100) peak all showed that the sample had characteristics of hard carbon after graphitizing at 2600°C.

The quantity of surface oxygen and nitrogen atoms both decreased gradually with temperature. Pyrrolic nitrogen (N-5) was the main combining style of nitrogen atoms at 1000°C, when the temperature reached 2600°C, oxygen atoms existed in the graphite sheet in the groups of quinoid carbonyl, ester and anhydrides, no nitrogen atom was detected.

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