

# Structural Determination of Pyrolyzed PI-2525 Polyimide Thin Films

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## Synopsis

Polyimide was pyrolyzed in an argon atmosphere at various temperatures, and thermally converted to amorphous carbon films. The irreversible change of polyimide under progressive heat treatment is characterized by three successive structural changes: pyrolysis, carbonization, and graphitization. X-ray photoelectron spectroscopy (XPS) studies show that the polyimide starts to dissociate at pyrolysis temperatures above 500°C. At temperatures higher than 650°C most functional groups of polyimide decompose to evolve gases from the sample. The polyimide then gradually becomes more carbon rich. It is believed that at pyrolysis temperature higher than 650°C the polyimide starts to form heterocyclic structures with residual oxygen and nitrogen incorporated into the heterocyclic carbon rings. X-ray analyses indicate that the polyimide at pyrolysis temperatures less than 1000°C is amorphous carbon and no long-term periodic structure can be detected. At pyrolysis temperatures higher than 2000°C, the polyimide is converted to microcrystalline graphite.

## INTRODUCTION

Carbon fibers have been prepared by thermal treatment of a large variety of polymeric precursors such as cellulose, rayon, polyacrylonitrile, and aromatic polyamides.<sup>1,2</sup> The polymer-based, high temperature-treated carbon fibers are used in high-performance composite materials in aeronautic and aerospace applications. Later pyrolysis studies on other polymers such as polyphenylene-1,3,4-oxadiazole, polyaminoquinones, and aromatic polyimide have focused on their conductivity properties.<sup>3-5</sup> High temperature pyrolysis of these aromatic-based polymers converts them from insulators to semiconductors and then to metallic-like conductors.<sup>6</sup>

Pyrolyzed polyimide is somewhat different from other graphitizable polymers such as polyacrylonitrile and rayon. The latter are usually heated to very high temperatures (over 2000°C), resulting in short, thin graphitized carbon fibers. In our experiment, the polyimide is pyrolyzed mainly at temperatures below 1000°C. The resulting pyrolyzed polyimide thin film is a highly conductive carbon-rich film which may be useful for applications requiring light weight, flat, chemical, and heat-resistant conducting materials, and it already shows a promising future in gas and radiation detectors.<sup>7</sup>

## MATERIALS AND METHODS

In our experiment, two kinds of commercially available polyimides (manufactured by DuPont de Nemours and Co) were used; PI-2525 polyamic

solution and Kapton. PI-2525 polyamic acid solution was used for XPS, X-ray, and Raman analyses. The polyamic acid solution was spin-cast on the substrate, followed by two drying and curing stages in a nitrogen atmosphere at 100 and 200°C each for 2 h, during which the polyamic acid was undergoing the imidization process. After 2 h at 200°C, the polyamic acid was fully cured and converted to polyimide. Kapton is a fully cured polyimide and was used for density and X-ray studies. Both polyimides are chemically identical and have the structure which was described in a previous paper.<sup>8</sup>

For pyrolysis, the polyimide sample was placed inside a small quartz tube oven, and low pressure argon gas was passed through the quartz tube. The argon gas was adjusted to approximately 5 cc/s flow rate. Gas flow was maintained at least 5 min to allow the system to reach steady state before heating began. The polyimide was brought to the desired pyrolysis temperature by setting a fixed heating rate (10°C/min). Usually, the pyrolysis temperature was in the range of 500–900°C. After the desired conditioning, the pyrolyzed polyimide was cooled down to room temperature under argon atmosphere to prevent possible oxidation and then removed from the furnace. The film was then ready for examination.

### Wide Angle X-Ray Analysis

Structural features of pyrolyzed polyimide were studied by wide angle X-ray analyses. From these analyses, one can determine at what pyrolysis temperature the pyrolyzed polyimide starts changing from amorphous state to microcrystalline graphite. Wide angle X-ray analyses were performed in the DIANO Diffractometer, using CuK $\alpha$  monochromatic radiation.

### Raman Spectroscopy Analysis

Raman studies can provide further information about whether the pyrolyzed polyimide is in amorphous or crystalline state. In our experiment, an Ar-laser was used to emit an intense laser beam with a fixed wavelength (488 nm). The emitted laser light passed through a lens and was focused on the pyrolyzed polyimide sample. The scattered Raman light was collected, passed through a monochromator, and detected by a photon counter. The final output was a plot of photonintensity (count) versus the wavenumber shift from the laser line.

### X-Ray Photoelectron Spectroscopy Analysis (XPS)

XPS analysis provides information on chemical states and elemental ratios of polyimide pyrolyzed at various temperatures. XPS analyses were performed on a Hewlett-Packard 5950B Electron Spectrometer, using a monochromatic AlK $\alpha$  X-ray source.

## RESULTS

### Apparent Density

The apparent density of polyimide pyrolyzed at temperatures between 700 and 900°C is plotted in Figure 1. It shows that the density of pyrolyzed polyimide increased from 1.49 to 1.57 g/cm<sup>3</sup>.

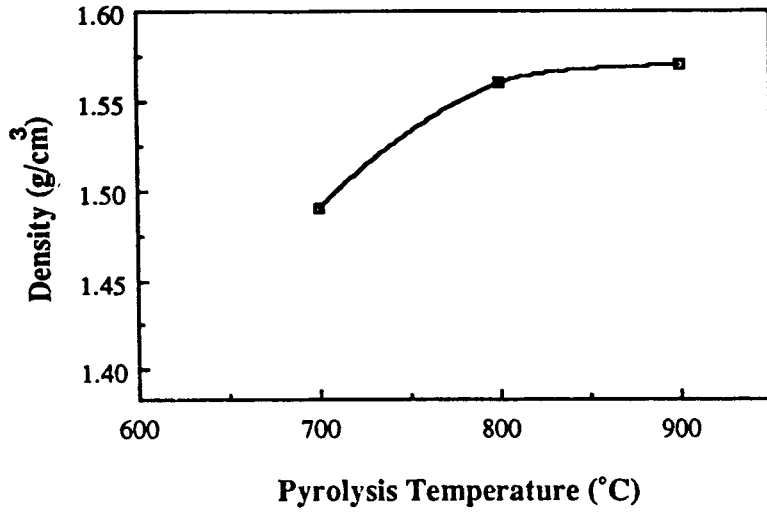


Fig. 1. Apparent density of polyimide film as a function of temperature of pyrolysis.

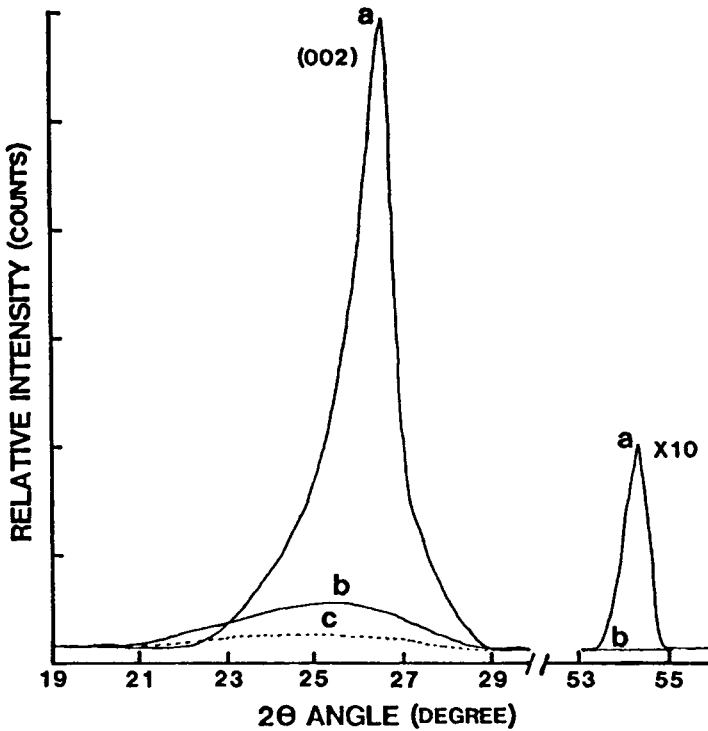


Fig. 2. Wide-angle X-ray diffraction of polyimide pyrolyzed at the temperatures noted: Line a: 2100°C, line b: 1500°C; line c: < 1000°C.

### X-Ray

In the X-ray diffraction experiments, the  $2\theta$  angle was swept from  $15^\circ$  to  $80^\circ$ . The results of X-ray diffraction are shown in Figure 2. Polyimides pyrolyzed at temperatures between  $500$  and  $900^\circ\text{C}$  showed no diffraction peak and only a very broad and weak peak appeared at  $2\theta$  angle from  $22^\circ$  to  $28^\circ$  (curve c in Fig. 2). For polyimide pyrolyzed at  $1500^\circ\text{C}$ , a diffuse amorphous carbon peak was seen in the  $2\theta$  angle between  $24^\circ$  and  $28^\circ$  (curve b in Fig. 2). For polyimide pyrolyzed at  $2100^\circ\text{C}$ , a strong but broad diffraction peak appeared at a  $2\theta$  angle equal to  $26.5^\circ$  and a much weaker diffraction peak appeared at  $2\theta$  equal to  $54.2^\circ$ . Both diffraction peaks are shown in Figure 2 curve a.

### Raman

The Raman spectra of polyimide pyrolyzed at  $700$ ,  $800$ , and  $900^\circ\text{C}$  are shown in Figure 3. All three pyrolyzed polyimide samples at different heat treatments showed almost identical Raman spectra. Two Raman peaks appeared at  $1640$  and  $1370\text{ cm}^{-1}$ . The intensity of the peak at  $1640\text{ cm}^{-1}$  was higher than the peak at  $1370\text{ cm}^{-1}$ .

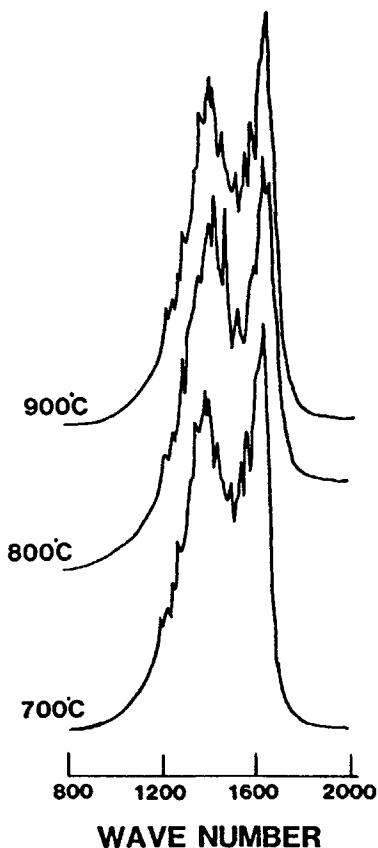


Fig. 3. Raman spectra of polyimide treated at  $700$ ,  $800$ , and  $900^\circ\text{C}$ .

## XPS

The detailed chemical state analysis of carbon, oxygen, and nitrogen of polyimide are shown in Figure 4. Polyimide has two carbon peaks at binding energies 288.3 and 284.6 eV, and has an unresolved carbon peak at binding energy 286.0 eV. The peak at 288.3 eV represents the imide carboxyl-type bonding and the peak at 286.0 eV represents C—O and C—N-type bonding.<sup>8</sup> The peaks at 288.3 and 286.0 eV decreased as the pyrolysis temperature increased. At temperatures above 650°C, the imide carboxyl-type carbon 1s peak disappeared and only weak and broad oxygen and nitrogen carbon 1s peaks near 286.0 eV coexisted with the strong C—C main peak. As temperature exceeded 900°C, only a graphite C—C main carbon 1s peak was seen and no oxygen and nitrogen-bonded carbon 1s peak was detected.

Polyimide has two oxygen peaks at binding energy 533.3 and 532.0 eV. The peak at 532.0 eV represents C=O-type bonding and the peak at 533.3 eV

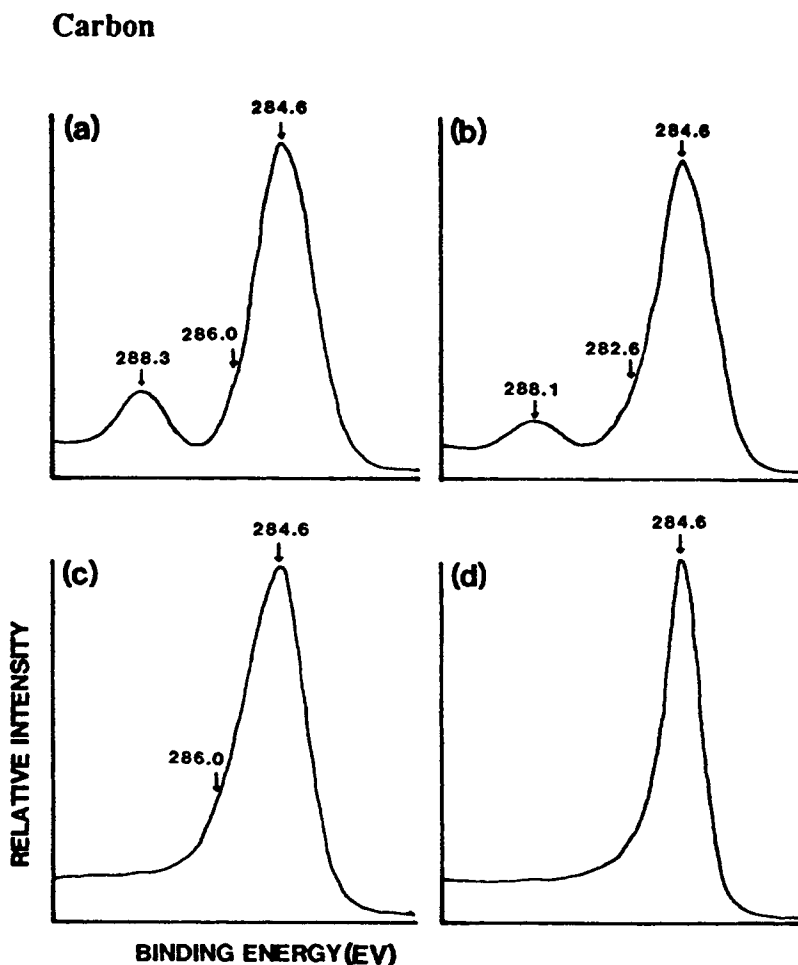


Fig. 4. Polyimide XPS narrow scan spectra of carbon, oxygen, and nitrogen 1s peaks: (a) raw material; after treatments at: (b) 600°C, (c) 650°C, and (d) 900°C.

## Oxygen

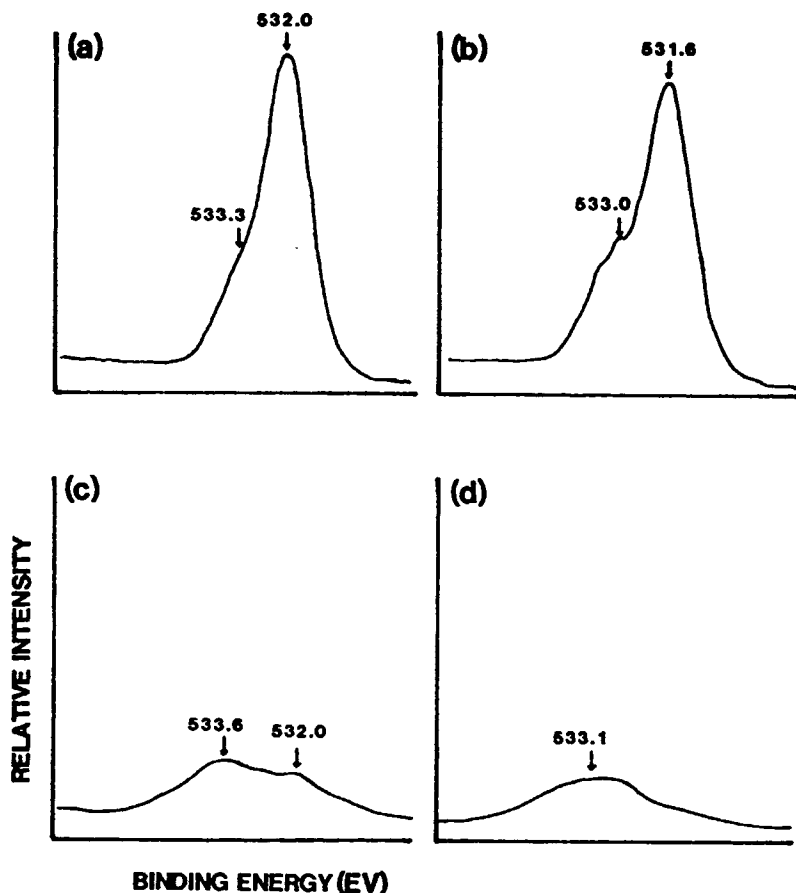


Fig. 4. (Continued from the previous page.)

represents C—O-type bonding.<sup>8</sup> The total oxygen content decreased as the pyrolysis temperature increased and became insignificant at temperatures higher than 900°C. The relative intensity of the C=O-type oxygen 1s peak decreased as the pyrolysis temperature increased. At 650°C both C=O and C—O-type oxygen peaks have the same intensity, and at above 650°C, these two oxygen peaks merged and became a very broad peak at 533.1 eV. At temperatures above 900°C this broad oxygen 1s peak became insignificant.

Polyimide has one nitrogen 1s peak at 400.5 eV. The peak at 400.5 eV represents the C—N-type nitrogen bonding.<sup>8</sup> A new nitrogen peak appeared at 398.5 eV at temperatures of 600°C. At pyrolysis temperatures above 600°C, the total intensity of the nitrogen peaks decreased sharply. At temperatures, above 650°C, both nitrogen peaks had the same relative intensity, and as the temperature reached 900°C, the two nitrogen 1s peaks become insignificant.

The theoretical elemental C : O : N ratio of polyimide is 76.0 : 17.4 : 6.9. XPS analyses showed the elemental C : O : N of polyimide was 77.5 : 16.5 : 6.0,

## Nitrogen

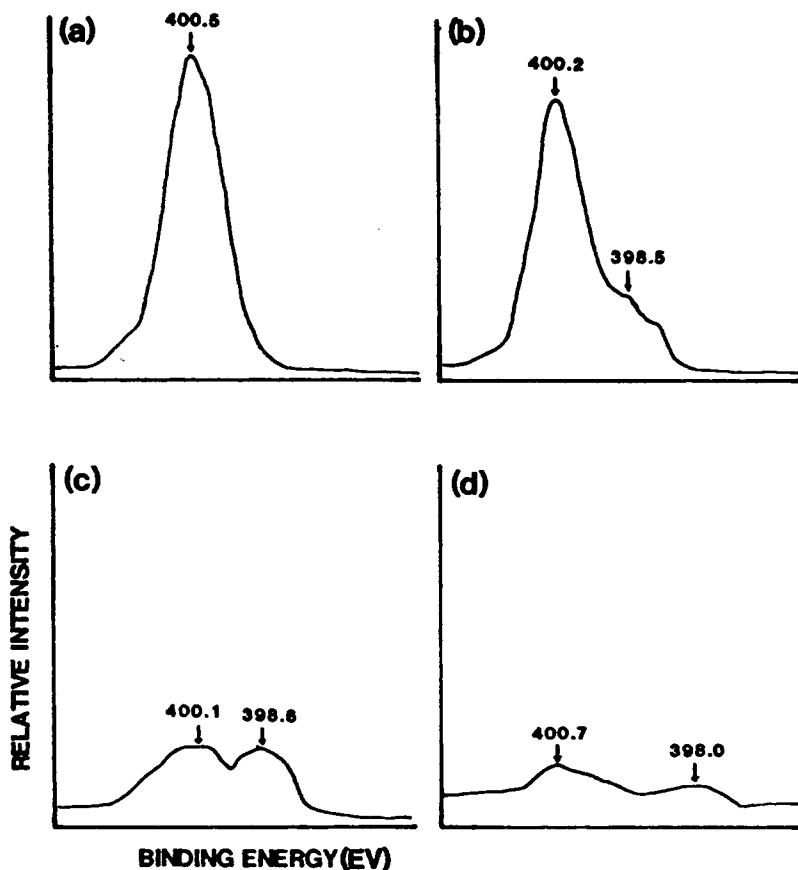


Fig. 4. (Continued from the previous page.)

which shows the XPS analyses indeed agreed quite well with the theoretical prediction.

The percent change of carbon, oxygen, and nitrogen in polyimide versus pyrolysis temperature is shown in Figure 5, and elemental compositions versus pyrolysis temperature are listed in Table I. Figure 5(a) shows that the carbon increased from 77.5 to 95.6% as the pyrolysis temperature increased from 450 (undissociated temperature) to 900°C. A step increase of carbon from 79.1 to 92.1% occurred between 550 and 650°C, and at temperatures above 700°C there was no significant increase in carbon content. Figure 5(b) indicates that the oxygen content decreased from 16.5 to 3.5% as the temperature changed from 450 to 900°C. A step change of oxygen content from 15.1 to 4.1% was observed as the temperature changed from 550 to 650°C. Figure 5(c) shows that the nitrogen content was constant at 6% at temperatures below 550°C, and started to decrease at temperatures higher than 550°C. The percent of nitrogen was changed from 5.8 to 0.9% as the temperature increased from 550

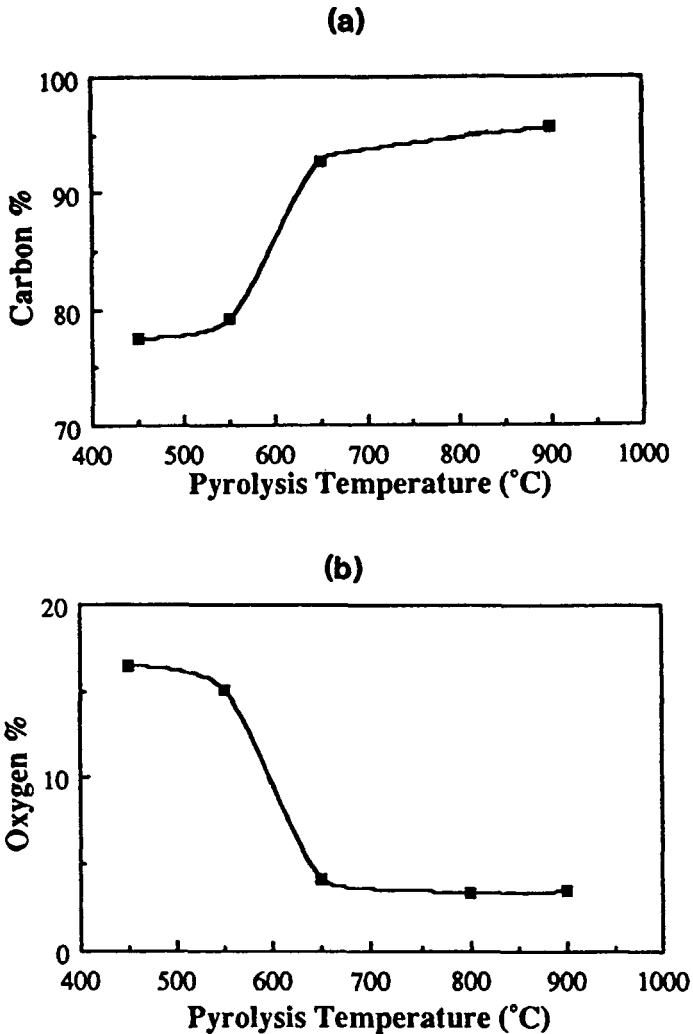


Fig. 5. The percent change in elemental carbon, oxygen, and nitrogen as a function of pyrolysis temperature for polyimide. (a) carbon, (b) oxygen, and (c) nitrogen.

to 900°C. At temperatures above 700°C no major changes of elemental composition were detectable.

## DISCUSSION

Pyrolysis studies of polymeric material such as polyacrylonitrile (PAN) always show that at high enough pyrolysis temperatures ( $> 2000^{\circ}\text{C}$ ), the polymer is converted to microcrystalline graphite.<sup>9</sup> X-ray studies of microcrystalline graphite show the interplane diffraction at (002) and two-dimensional lattice diffractions at (10) and (11). The  $2\theta$  angle for (002) diffraction is about  $26.5^{\circ}$ , for second-order (002) diffraction about  $54.2^{\circ}$ , for (10) about  $44.5^{\circ}$ , and for (11) about  $78^{\circ}$ .<sup>10</sup>



(c)

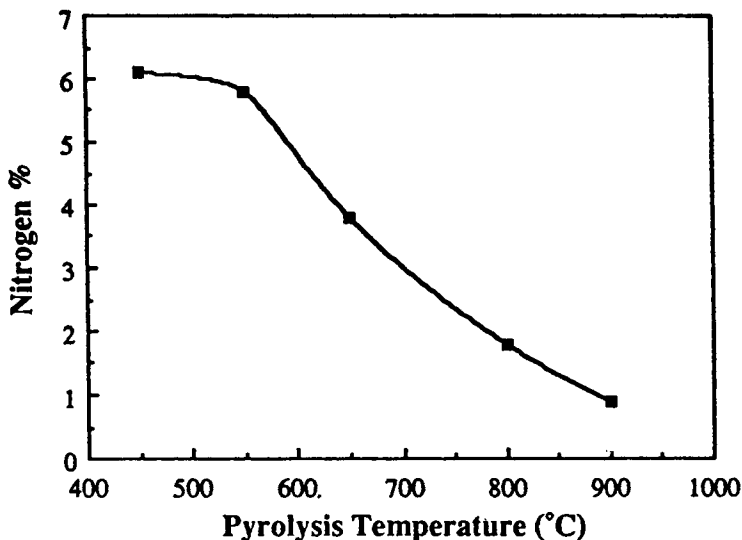


Fig. 5. (Continued from the previous page.)

TABLE I  
Elemental Ratio of Pyrolyzed Polyimide at Different Pyrolysis Temperatures

Pyrolysis temp. (°C)	C	O	N
450	77.5	16.5	6.0
550	79.1	15.1	5.8
650	92.1	4.1	3.8
800	94.8	3.4	1.8
900	95.6	3.5	0.9

X-ray studies of polyimide pyrolyzed at different temperatures show that at temperatures less than 1000°C the material is in an amorphous state.<sup>11,12</sup> The polyimide undergoes reorganization of short-range order of heterocyclic carbon ring units incorporating a small percent of residual oxygen and nitrogen. It is believed this local structural reorganization of heterocyclic carbon rings begins to form dense heterocyclic carbon domains (graphitic domain) with strong  $\pi$ -orbital overlap in the amorphous carbon matrix. No long-range ordered graphite layer structure has been observed and the inhomogeneity of polyimide due to the growing of graphitic domains cause the conductivity of pyrolyzed polyimide to increase into the semiconductor range.<sup>13</sup> At temperatures above 1500°C, continuous growing of graphitic domains with increasing size of layer structure causes further increases in conductivity.<sup>13</sup> The pyrolyzed polyimide in this stage is an inhomogeneous amorphous carbon. At temperatures above 2000°C, graphitization is complete, and the pyrolyzed

polyimide becomes microcrystalline graphite. The "apparent" size of the graphitic layer estimated by the Scherrer formula is in the range of 70 Å. The pyrolyzed polyimide in this stage is no longer amorphous carbon; the entire carbon matrix is polycrystalline graphite.<sup>14-16</sup> The lack of (hk) diffraction may be caused by the following: Higher disorder and defect density along the (hk) planes, structural fluctuation of (hk) planes, and random organized layer structure. All these factors may make the intensity of (hk) diffractions become too weak to be detected by the X-ray diffractometer.

Other evidence that pyrolyzed polyimide is still an amorphous carbon at pyrolysis temperatures less than 1000°C is by Raman analyses. Vidano and Fischbach<sup>(17)</sup> show the Raman spectrum for crystalline graphite has two strong peaks at 2700 cm<sup>-1</sup> and 1580 cm<sup>-1</sup>, and one weak peak at 1360 cm<sup>-1</sup>. The Raman peak at 2700 cm<sup>-1</sup> is sensitive to the crystallinity of the graphite; this Raman peak is not detectable for amorphous carbon. The Raman spectrum for amorphous carbon shows two Raman peaks; one at 1620 cm<sup>-1</sup> and the other at 1360 cm<sup>-1</sup>.<sup>17</sup> In graphite the Raman peak at 1580 cm<sup>-1</sup> is caused by in-plane vibrations of the layer.<sup>18,19</sup> In amorphous carbon this peak still exists but becomes broadened and shifted to above 1600 cm<sup>-1</sup>. The Raman peak at 1360 cm<sup>-1</sup>, which exists in both crystalline graphite and amorphous carbon, is also associated with in-plane vibrations and results from structural imperfections and finite graphite size.<sup>20-22</sup>

The Raman spectra of polyimide pyrolyzed at temperatures ranging from 700 to 900°C are very similar to the amorphous carbon.<sup>17</sup> The Raman peaks of polyimide at various pyrolysis temperatures all show two Raman peaks; one at 1640 cm<sup>-1</sup> and the other at 1370 cm<sup>-1</sup>. These peaks are almost identical to the peak positions of the amorphous carbon. The relative peak intensity between these two peaks is very similar for both pyrolyzed polyimide and for amorphous carbon. It is believed that polyimide pyrolyzed at temperatures below 1000°C is amorphous carbon with a small percent of oxygen and nitrogen incorporated into the heterocyclic carbon rings. The microcrystalline graphite-like domains at this temperature are still insignificant but the growing graphitic domains have started to form microinhomogeneities in the pyrolyzed polyimide matrix.

Previous thermogravimetric studies indicate that the polyimides dissociate at temperatures between 500 and 600°C.<sup>8</sup> At temperatures above 600°C, the weight loss rate slows and finally becomes insignificant above 700°C. The corresponding ESCA data show that most imide carbonyl functional groups indeed disappear at 600°C and the remaining oxygen is incorporated into the aromatic carbon rings and possibly form either quinone (—C=O) or bridging aromatic ether types of bonding with the graphitic carbon rings. A large decrease of C—N-type nitrogen above 600°C and the appearance of a new peak at 398.5 eV indicate that the nitrogen loss has started and the remaining nitrogen has either formed aromatic C—N-type bonding or has been conjugated into the aromatic carbon ring networks.<sup>3</sup>

Both ESCA and weight loss data show no significant weight loss or elemental ratio change at pyrolysis temperature between 700 and 900°C. This data indicates that the polyimide chain dissociation is nearly complete at temperatures higher than 700°C. The increasing density in this temperature range indicates that the remaining aromatic carbon rings in the pyrolyzed

polyimide may be starting to recombine to form a larger and denser heterocyclic network. For temperatures higher than 1500°C, the ESCA data show no nitrogen component and only a few percent of remaining oxygen. The remaining oxygen is either due to the oxygen incorporated into the heterocyclic carbon rings or to carbon oxidization during the pyrolysis.<sup>23</sup> Since the oxygen content decreased as the pyrolysis temperature increased, the major part of the remaining oxygen is most likely due to oxygen incorporated into the heterocyclic carbon rings network.

## CONCLUSIONS

Experimental analyses indicate that when polyimide is pyrolyzed, its functional groups are broken below 650°C. This chemical evolution is characterized by the presence of strong electron paramagnetic resonance signals associated with unpaired electrons due to the existence of broken bonds (described in detail in Ref. 23). The pyrolyzed polyimide in this stage is a low (less than 90%) carbon content amorphous material. Above 700°C weight loss is insignificant. Some oxygen and nitrogen is incorporated into the heterocyclic carbon rings or is continuously released from the sample. From density and X-ray studies, it is believed that those heterocyclic carbon rings rearrange or recombine to form larger and denser heterocyclic carbon ring networks. Inhomogeneity of the pyrolyzed polyimide will occur when those metallic graphitic domains start to appear in the amorphous matrix. Raman and X-ray studies show that the polyimide at low pyrolysis temperature (less than 1000°C) is still an amorphous carbon with high carbon content (greater than 96%). The inhomogeneity of the material causes the increase of conductivity, described in detail in Ref. 23. Finally, at pyrolysis temperatures higher than 2000°C, the polyimide becomes microcrystalline graphite.

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