



## Characterization the Composite Polyimide Films with Nickel after Heat Treatment

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### Abstract:

Characterization of the polyimide-based composite films containing carbon particles was studied and the kinetics of the initial stage of carbonization and the effect of the filler on the properties of the carbonized films were evaluated. Two polyimide (PI) characterized by different rigidity and different degrees of ordering of the intermolecular structure were used. The character of the particles action on the kinetics of the carbonization process depends on the heating rate. In this work, we demonstrated the incorporation of different foreign elements into carbon films by mixing a Nickel with a poly (amic acid) in solution followed by heat treatment. It was found that Nickel in the polyimide film promotes the carbonization of matrix polyimide and also an increase of the electrical conductivity and magnetic property of the films. The growth of metal particles in carbon films and the change from paramagnetic to ferromagnetic behavior were observed with the increase of carbonization temperature. Here in, a polyimide film containing Nickel of 0.6 at% of the total number of atoms in the precursor mixture and heat-treated films were investigated in some detail. Systematic measurements of X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman are used. That showed the quantitative changes of structure and property with carbonization

**Keywords:** heat treatment, Nickel-polymer complexes, polyimides



## 1. Introduction

As a high-performance engineering plastic materials, polyimide (PI) is well known and intensively studied for its excellent thermal and mechanical properties. The PI-based materials have been widely used in industrial applications such as aircraft parts, aerospace applications, electronic packaging, adhesives, and matrix materials for composites.<sup>1-6</sup> Since 1970s, Burger found that the carbon film derived from Kapton<sup>®</sup> had a graphitizing nature.<sup>7</sup> A great deal of work has been done to focus on the fabrication of carbon materials using PI as a precursor by extremely high thermal treatment, and the results show that PI is a promising candidate for the carbonization process due to its higher carbon content and rigid aromatic structure, which can easily form ordered carbon or graphite layer structures.<sup>8-10</sup> In order to get a regular structured carbon material with the expected properties, a larger number of efforts have been made for better carbonization of polymers in recent two ways. The first study focuses on improving the degree of orientation of polymeric chains. The other work focuses on the incorporation of different foreign elements, i.e., transition metal or metal oxide particles. This is because that the crystallinity of carbon as materials can be enhanced due to the catalytic effect of metal particles and the heat-treatment temperature can also be reduced.<sup>11,12</sup> Moreover, the electrical or magnetic properties of the carbons materials might be improved by the implantation of metal particles.<sup>13,14</sup> For explorations on the catalytic effect of nickel particles, Bin et al. added them into PI films to improve the degree of graphitization, and the electric conductivity of the resulting carbon film reached 1000 S/cm.<sup>15</sup> Additionally, the commercially available PIs with different chemical structures such as Kapton<sup>®</sup>, Upilex<sup>®</sup>, and Novax<sup>®</sup> products have already been studied, finding that the graphite films with a high degree of graphitization, high electrical conductivity, and very low anisotropy ratio can be achieved.<sup>7,9,10</sup> The researches



on the carbonization of PI films with different chemical structures indicated that the rigid structure of the repeating unit played an important role in the carbonization process when using polyimide as a precursor.<sup>16</sup> In our previous study, an metal complex( iron) was incorporated into the PI materials synthesized from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) for the promotion of carbonization process.<sup>19</sup> The results showed that the final product both exhibit good electrical and magnetic properties. This makes us believe that, by using PI films synthesized from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and p-phenylenediamine (PDA) which possesses a more rigid molecular structure and with the help of metal catalyst, it is possible to get a better carbon film with excellent electrical and magnetic properties. The purpose of this study is to discover both the structural influence and the catalyst effect on the preparation of carbon films from PI films. The PI films used in this work were synthesized from BPDA, DMA and PDA. Nickel is incorporated as the catalyst by the in-situ method to get a homogeneous dispersion. The microstructure transition of PI molecules and the change of metal particles were tracked. In the present work, the carbonization process film is studied by measuring the changes in size, weight, and chemical composition with carbonization, and by structure analysis, electrical conductivity and Magnetic properties measurement on the carbonized film, therefore, nickel was selected. They were heat-treated at different temperatures between 600 and 1600C°.

## 2. Experimental

### 2.1. Materials

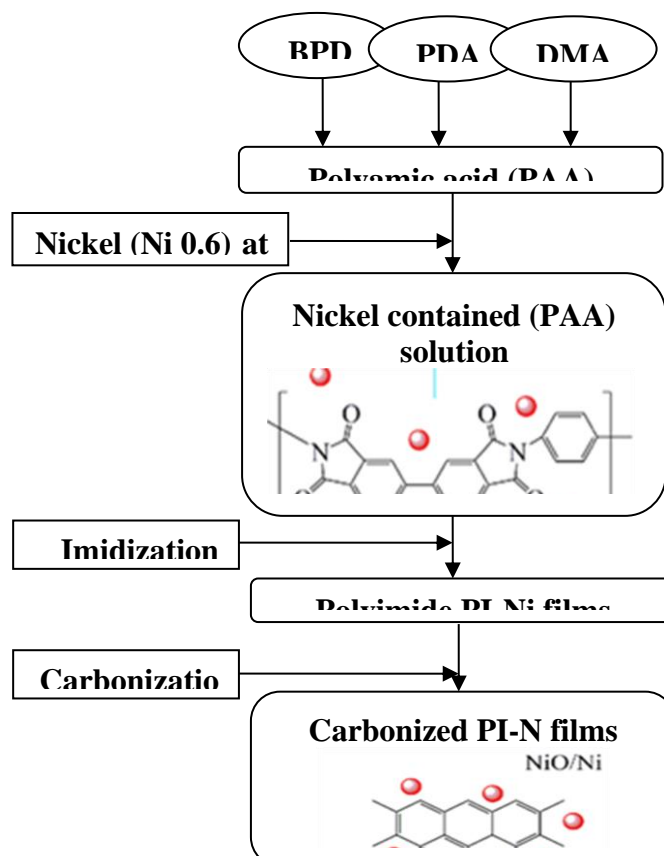
BPDA was provided by Wuxi Bohai Chemical Products Co., Ltd. PDA was purchased from Shijiazhuang Haili Fine Chemical Co., Ltd. N, N-dimethylacetamide (DMAc, analytical pure, 99.9%) was provided by Tianjin Guangfu Fine Chemical Research Institute. Nickel acetate tetrahydrate was



provided by Sinopharm Group Co., Ltd. All chemicals were used as raw materials without purification.

## 2.2. Preparation of PI-Ni composite film

The synthesis procedure for the preparation of PI, or PI-Ni composite films is shown in Fig.1. The content of nickel, according to the previous literature, was chosen as 0.6 at% (atomic percentage) in the precursor mixture (PAA and nickel acetate tetrahydrate).<sup>17</sup> After continuously stirring for 30 min at least, the mixture was cast on a clear glass plate. Then, the composite film was heated in an air atmosphere at 80°C for 20 min and at 100°C, 200°C, 300°C, and 320°C, each for 1 h, yielding the PI film containing nickel. The thickness of the resultant composite film was approximately 40µm and the color was dark brown. The PI-Ni composite film, in which nickel acetate tetrahydrate dissolved in ethanol was used as a Ni precursor. For a contrast, pure polyimide film without nickel particles was also prepared.





**Fig.1.**The procedure of preparation of carbon films derived from PI, PI-Ni composite

### 2.3. Carbonization of PI and PI-Ni composite films

The carbonization process was performed under a nitrogen atmosphere in a tubular furnace. The thermal-treated PI and PI-Ni films were sandwiched between polished artificial graphite plates and heated to 600°C, 800°C, 1000°C, 1200°C, 1400°C, and 1600°C respectively and held at the final temperature for 1 h. The heating rate of all samples was 5 °C/min. The PI-Ni films after carbonization at 600°C, 800°C, 1000°C, 1200°C, 1400°C, and 1600°C under a nitrogen flow were denoted as PI-Ni-600, PI-Ni-800, PI-Ni-1000, PI-Ni-1200, PI-Ni-1400, PI-Ni-1600, respectively, the same as the PI film.

### 2.4. Characterization

The structure and crystallinity of carbon films were characterized by X-ray diffraction (XRD). The XRD patterns were obtained with an X-ray diffractometer (D8 ADVANCE, Bruker AXS, Germany) using Cu K $\alpha$  radiation ( $\lambda= 0.154$  nm) and operated at 40 kV and 200 mA with a scan rate of 0.18° per second in the range of 10–90° (2 $\theta$  value). A Hitachi S-4700 scanning electron microscope (SEM) operating at an accelerating voltage of 20 kV was used to observe the surface morphology of the carbon films. The electrical conductivity and magnetic properties of the composite films were measured by a four-point-probe (FPP) device and vibrating sample magnetometer (7410VSM, Lake Shore, America), respectively.

## 3. Results and discussion

### 3.1. XRD measurement

The effects of the carbonizing temperature on the crystal structures of carbon films derived from PI films, and PI-Ni films were identified by XRD. The diffraction patterns for the carbon films derived from pure PI film are shown in



Fig. 2a. The pattern of PI has two small peaks at  $2\theta=20.04^\circ$  and  $25.38^\circ$ , which indicates that PI film without carbonization has relatively low crystallinity. The (002) line of the carbon films derived from PI film becomes sharper and shifts to higher angles with increasing the carbonization temperature, which is due to the formation of well-regulated structure. Meanwhile, a small peak appears at around  $2\theta=43^\circ$  for the PI films after heat treatment and becomes more apparent with increase of the carbonizing temperature, which is the same with the characteristics of graphite.<sup>18</sup>

The structural change of PI-Ni film during the carbonization process is illustrated in Fig. 2b. In theory, nickel complex can transfer to amorphous carbon and NiO after heat treatment at  $400^\circ\text{C}$  in air and then transfer to crystalline carbon and Ni at  $600^\circ\text{C}$  or above.<sup>20</sup> However, no extra peaks in the PI-Ni films appear by comparison with PI films at  $1000^\circ\text{C}$  or less. This is due to the overlap of the (10) reflection of carbon and the (111) reflection of metallic nickel and the (202) reflection of nickel oxide at about  $2\theta=44^\circ$ .<sup>21,22</sup> When heated up to  $1200^\circ\text{C}$  or above, two peaks at  $44^\circ$  and  $52^\circ$  develop with increasing carbonizing temperature, indicating that more and more metallic Ni is appearing.<sup>11</sup> It is evident that the peaks at  $44^\circ$  and  $52^\circ$  are attributed to plane (111) of metallic Ni and plane (004) of carbon, respectively. In addition, the (002) reflection of graphite carbon in PI-Ni film becomes narrower and sharper than that of PI film at the same condition. This confirms that the nickel particles can accelerate the carbonization process of PI film.

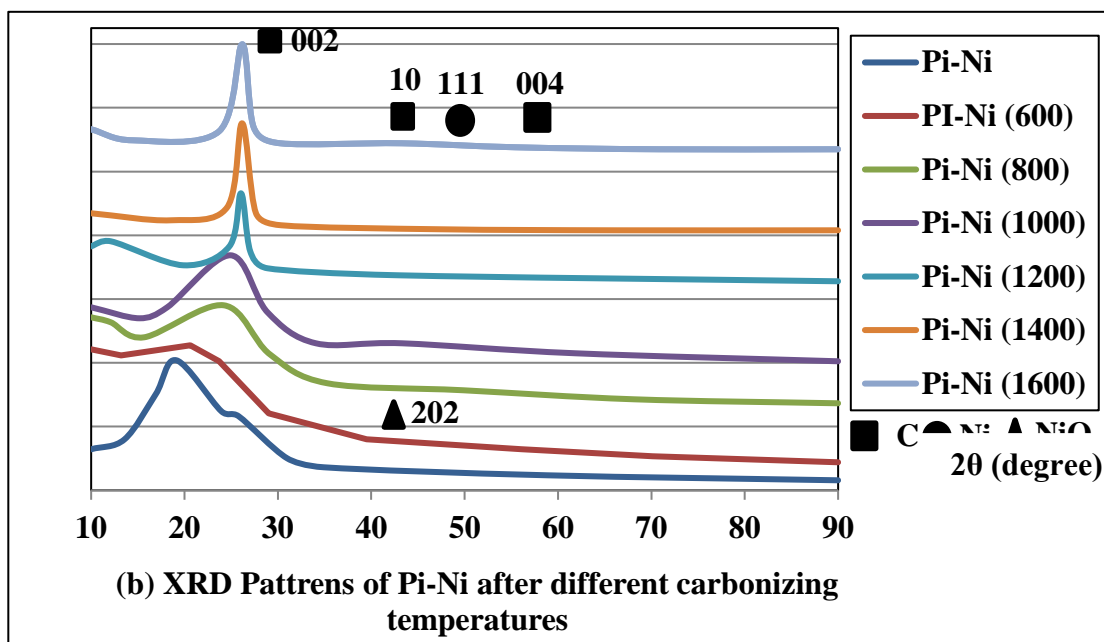
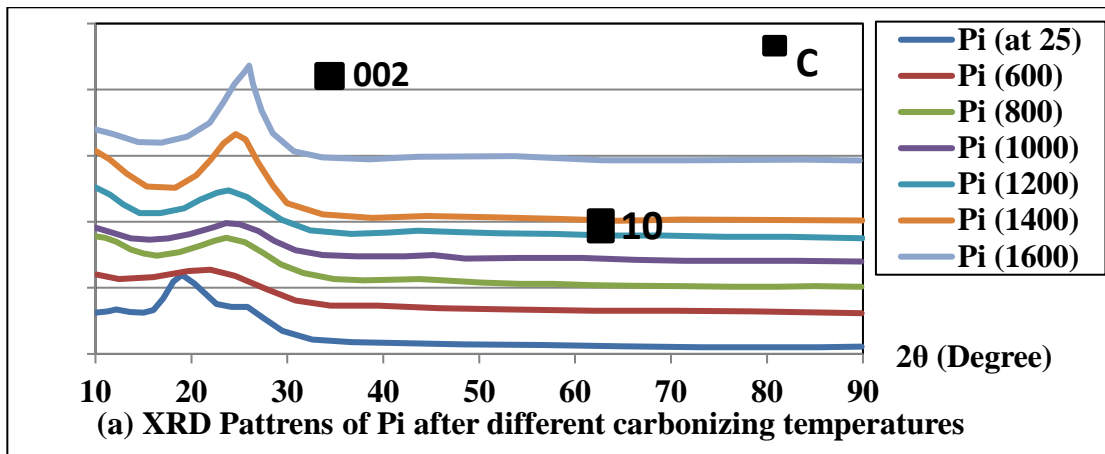


Fig. 2 XRD patterns of PI & PI-Ni films with different carbonizing temperatures.

### 3.2. SEM of PI and PI-Ni composite films with different carbonization temperatures

SEM measurements have been applied to observe the surface morphology of various films. Fig. 3a-d describes the surface morphology of PI films treated by different carbonization temperatures. The surface of PI film exhibits smooth and flat without any defects. With the increase of the carbonization temperature, the carbon films present a more rough surface morphology at the temperature lower than 1200°C. This is ascribed to the release of gas caused by the pyrolysis





of PI film. However, it is interestingly noted that the surface of PI-1600 film shows a smooth surface with a microporous structure, indicating that the rearrangement of molecular structure takes place after the violently pyrolysis of PI film.

Fig. 3i-l show SEM photographs of the PI-Ni film and the heat-treated ones. For the films treated at temperatures lower than 600°C (Fig. 3i-j), no images of particles can be observed, which may be due to a small number of nickel complexes. It is clearly observed that some particles with a size of 200~900 nm in diameter appear on the surface of PI-Ni-1200 film (Fig. 3k). These particles are considered as metallic nickel based on XRD analysis. Meanwhile, we can deduce that metallic nickel does not generate at 600°C, indicating that there is no (111) reflection of metallic nickel at  $2\theta=44^\circ$  in XRD curve of PI-Ni-600. When heated up to 1600°C (see Fig. 3l), we can not observe porous carbon structure due to carbonization of the PI matrix, but some defects can be

found due to the presence of metallic nickel. Additionally, some nickel particles are incorporated into carbon layers. This indicates that the increase in the number of metallic nickel may be beneficial to dense packing of carbon layer.

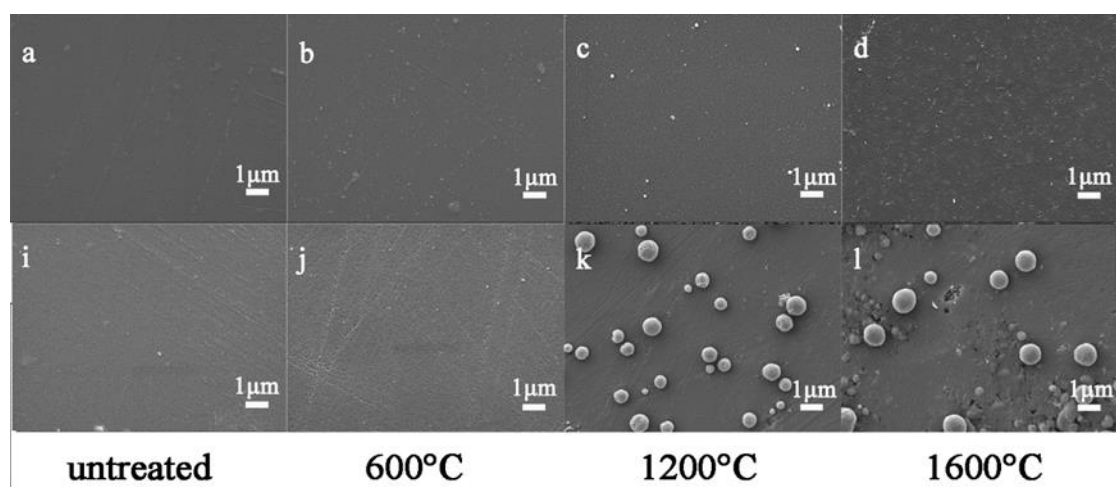


Fig. 3 SEM images of PI (a-d), PI-Ni (i-l) films carbonized at the indicated temperatures.





### 3.3. Electrical conductivity

The electrical conductivity of carbon films was first measured, and the variation trend of the surface resistivity depending on carbonization temperature is depicted in Fig. 4. At carbonization temperatures lower than 600°C, the sheet resistivity of all the carbon films is too high to be measured. This may be caused by the high resistance of polyimide matrix. Above 800°C, the surface resistivity's of all the carbon films decrease with an increase of the carbonization temperature due to the formation of carbon layer structure. In addition, the surface resistivity of all the carbon films containing iron or nickel is less than that of pure PI especially at low carbonization temperatures. At 1400°C, all the carbon films present almost the same resistivity, as shown in Table 1. This indicates that nickel complex have a catalytic effect on the carbonization of the composite films.

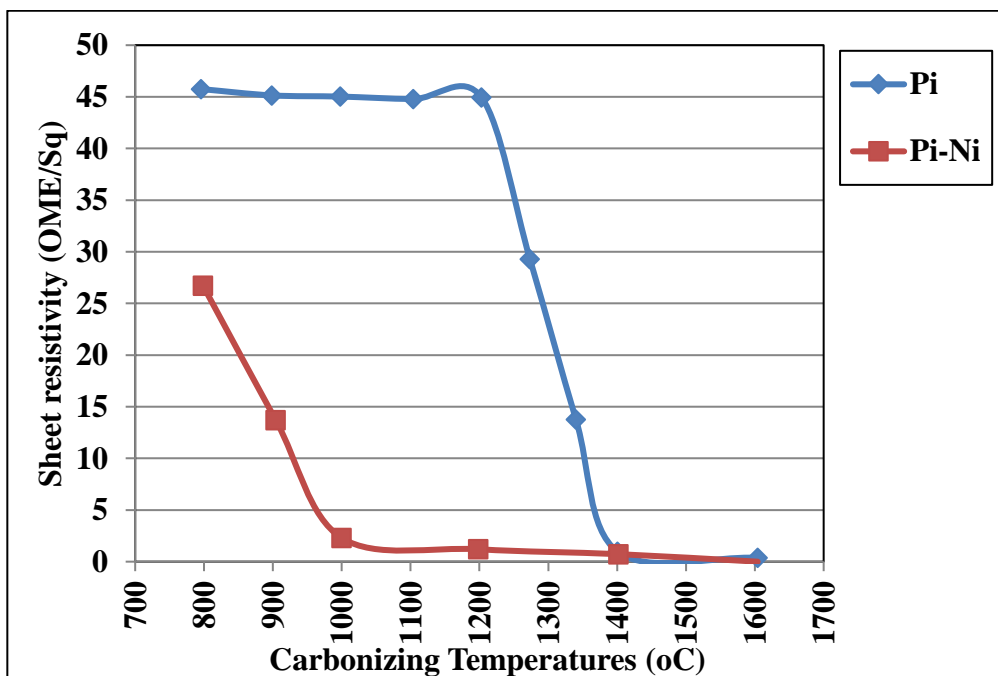


Fig. 4 Variation of surface resistivity of carbon films with carbonization temperatures

**Table 1** Sheet resistivity of carbon films with different carbonization temperatures



Specimens	Sheet resistivity ( $\Omega/\text{sq.}$ )				
	800°C	1000°C	1200°C	1400°C	1600°C
PI	45.58	45.07	44.72	0.80	0.55
PI-Ni	26.62	2.30	1.38	0.82	0.49

### 3.4. Magnetic properties

The magnetic behaviors of PI and PI-Ni carbon films at different carbonization temperature can be observed from the magnetic hysteresis curves shown in Fig. 5. In these magnetic hysteresis curves, the curves of PI and PI-Ni carbon films did not exhibit hysteresis any more, and the magnetization changed almost linearly with the applied magnetic field. The  $M_s$ ,  $M_r$  and  $H_c$  values of different carbon films are given in Table 2.

**Table 2.** Magnetic properties of the carbon films

Sample	$M_s$ (emu/g)	$M_r$ (emu/g)	$H_c$ (oe)
PI	0.16864	0.0086256	198.36
PI-800	0.10052	0.0069042	296.03
PI-1600	0.13876	0.014874	266.69
PI-Ni	0.41911	0.018675	144.34
PI-Ni-800	0.45798	0.022401	145.97
PI-Ni-1600	0.44571	0.023703	152.75

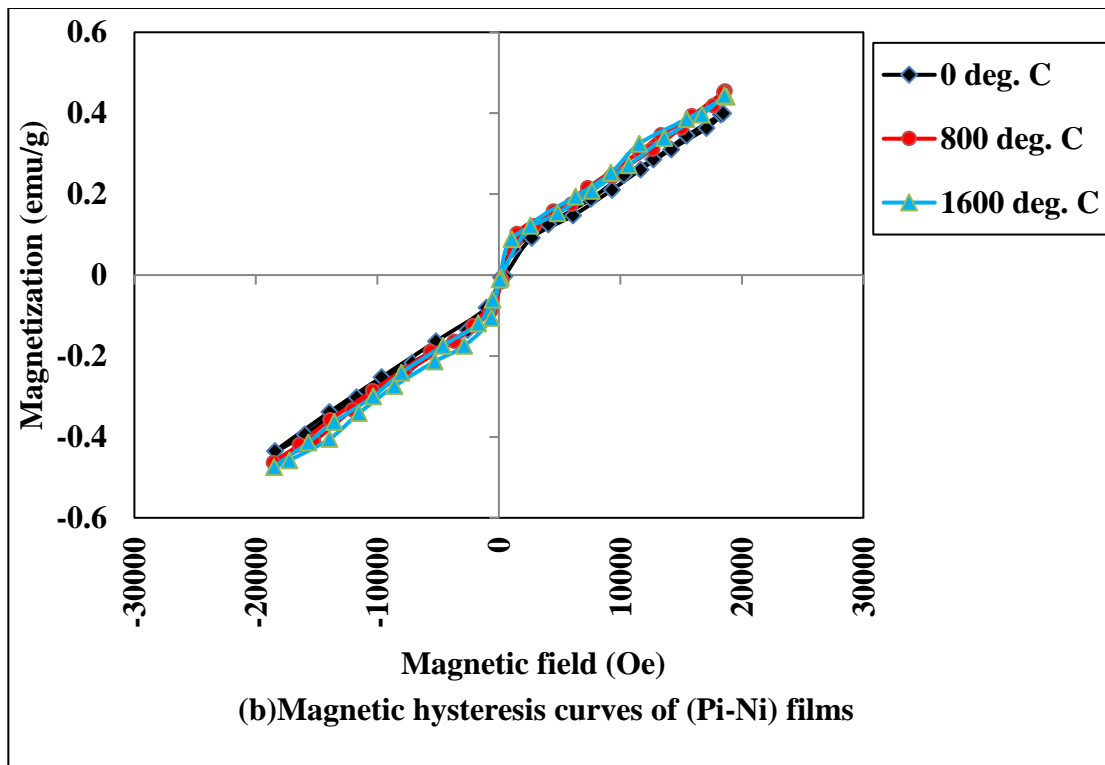
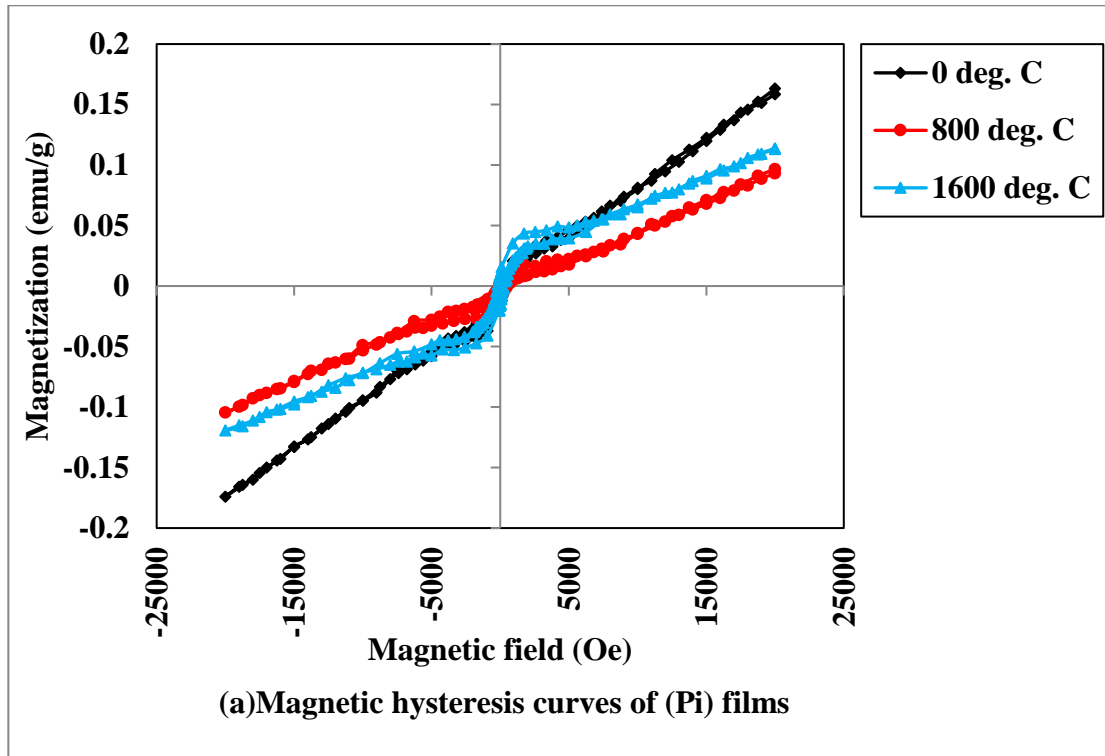


Fig. 5 Magnetic hysteresis curves of (PI) & (Pi-Ni) carbon films



#### 4. Conclusion

The carbon film was obtained by carbonizing heat treatment kinds of polyimide with nickel film prepared through process from 600 to 1600°C in a nitrogen atmosphere. During heat treatment, the oxygen within the PI film was mainly released in the temperature range of 600–700°C due to the evolution of CO and CO<sub>2</sub>, the combination of metal particles with carbon films was successfully carried out by using polyimide and metal complexes. The change of nickel clusters in the film occurred remarkably during carbonization in the temperature range of 600–1600 °C, which is in good accordance with SEM observations on the same films. The presence of the metal catalyst promoted the carbonization of matrix polyimide and resulted in high electrical conductivity. After treatment at 1600°C, there was almost the same conductivity for the nickel-containing carbon films and carbon films derived from pure PI as a result of the compensation of the crystalline improvement in the matrix carbon resulting from the pore formation due to the reduction of nickel compounds. The detailed analyses of chemical and physical variations of film during carbonization and comparison of carbonization processes for the different carbon precursors indicate that the polyimide with nickel is a good candidate for the manufacture of carbon film.



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