

Effect of Ferrous metal on The Electrical Conductivity and Growth of Metal Particles after Carbonization for Polyimide Films

Dr. FathiEtaher Elbakoush¹, Dr.Mohamed EmhamedAbosaf²

^{1,2}(Mechanical Department, Om Alrrabia college of sciences and Technology, Libya)

Abstract:

In heat treatment, carbonization is essential to improve the charactrcts of materials. In this work, Polyimide(PI) and polyimide –metal(PI-Fe) films have been carbonized under different degrees of temperature.Polyimide-metal composite films were carried out by mixing a Ferrum complex with polyimide in solution having been prepared by poly amic acid (PAA). The aim was to investigate the effect of the adding metal on the electrical conductivity and growth of the metal particles in Polyamide-metal films after carbonization.The properties of the synthesized polyimide heat-treated film containing 0.6 % of metal(Fe) were completely investigated by X-ray diffraction (XRD), scanning electron microscopy(SEM), transmission electron microscopy (TEM), the four-point-probe device (FPP) and vibrating samplemagnetometer (VSM).It was found that the metal in the polyimide film promotes the carbonization of matrix polyimide and also an increase of the electrical conductivity 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.

Key Word: polyimide film; carbonization; Polyimide-metal composite; electric; magnetic.

Date of Submission: 01-08-2020

Date of Acceptance: 16-08-2020

I. Introduction

Polyimide (PI) is important in engineering plastic materials field, for that, it is well known and intensively studied for its excellent thermal and mechanical properties, and has been widely used in industrial applications such as aircraft parts^[1], aerospace applications^[2], electronic packaging^[3], adhesives^[4], and matrix materials for composite materials^[5-6]. In the 1970s, Burger et alhad found that carbon film derived from Kapton had a graphitizing nature^[7]. Many studieshave shown that PI was used to fabricate carbon materials by a higher thermal treatment, and the results show that PI is a promising candidate for the carbonization process due to the higher carbon content and the rigid aromatic structure, which can easily form ordered carbon or graphite layer structures^[8-10].

In order to get a regular structured carbon material with the expected properties, great efforts have been made for better carbonization of polymers in two ways. The first one concentrated on improving the degree of orientation of the polymer chains. The other way focuses on the incorporation of different foreign elements, i.e. transition metal and metal oxide particles. This is because it is reportedthat the crystallinity of the carbon materials can be enhanced due to the catalytic effect of the metal particles, and the heat-treatment temperature can also be reduced^[11-12]. Moreover, the electrical or magnetic properties of the carbonized materials might be improved by the implantation of metal particles^[13-14]. For explorations on the catalytic effect of Nickel particles, Bin et aladded them into PI films to improve the degree of graphitization and the electric conductivity of the carbonized film reached 1000 S/cm^[15]. As for metal oxide, Zhou H et alprepared PI/Fe₃O₄ composite microspheres using a facileone-step solvothermal method and found that the composite microspheres both showed excellent thermal stability and protected the magnetite core from oxidation^[16]. Oka et alfound that the presence of Ferrum could promote the carbonization of matrix polyimide and increase the electrical conductivity^[17]. Additionally, commercially available PIs with different chemical structures such as Kapton^[8], Upilex^[9], and Novax^[10] products have already been studied, finding that graphite films with a high degree of graphitization and high electrical conductivity can be achieved. Research on the carbonization of PI films with different chemical structures indicates that the planarity and orientation of the repeating unit play an important role in carbon film derived from polyimide^[18]. In theory, pyromellitic dianhydride (PMDA)/ oxydianiline(ODA) has the highest planarity compared with other systems of polyimide and is supposed to give carbon film with high performance. However, PMDA/ODA is so rigid that it is comparatively difficult to prepare.

Therefore, the purpose of this study is to combine both the influence of the structureand the catalyst effect on the carbonization behavior of the PI films. The PI films used in this work were prepared from poly-

biphenyl dianhydride (BPDA) and para-phenylenediamine (PDA). Ferrum complex were incorporated as the catalyst by the in-situ method to get a homogeneous dispersion. The microstructure transition of PI molecules and the growth of metal particles were investigated and the electrical and magnetic properties of the derived carbon films were then carefully studied.

II. Material And Methods

Materials: Poly-biphenyl dianhydride (BPDA) was provided by Wuxi Bohai Chemical Products Co. Ltd. Para-phenylenediamine (PDA) was purchased from Shijiazhuang Haili Fine Chemical Co. N,N-dimethyl acetamide (DMAc, analytical pure, 99.9%) was provided by Tianjin Guang Fu Fine Chemical Research Institute. Ferrum (III) acetylacetonate (AAI) was provided by Shanghai Suocheng Chemical Co., Ltd. Nickel acetate tetrahydrate was provided by Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as raw materials without purification.

Preparation of PI-Fe composite film: The synthesis procedure for the preparation of PI, PI-Fe composite films is shown in Figure no.1. In a typical process, PDA was first dissolved into DMAc and then BPDA was gradually added into the solution under an ice

water bath to prepare PAA solution. This was followed by the introduction of a solution of Ferrum (III) acetylacetonate (AAI) in DMAc. The content of Ferrum, according to the previous literature^[19], was chosen as 0.6at % (atomic percentage) in the precursor mixture (PAA and Ferrum (III) acetylacetonate). After continuous stirring for at least 30min, the mixture was cast on a clear glass plate. Then the composite film was heated in air atmosphere at 80°C for 20 min and at 100°C, 200°C, 300°C, and 320°C, each for 1h, yielding PI film containing Ferrum, during which thermally oxidated Fe³⁺ ions transferred to Fe₃O₄. The thickness of resultant composite film was approximately 40µm and the color was dark brown. For contrast, pure polyimide film without Ferrum was also prepared



Figure no 1:the synthesis procedure for the preparation of carbon films derived from PI, PI-Fe composite film

Carbonization of PI-Fe composite film:

The carbonization proceeded under nitrogen atmosphere in a tubular furnace. The thermal-treated PI-Fe film 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. PI-Fe films after carbonization at 600°C, 800°C, 1000°C, 1200°C, 1400°C, and 1600°C under nitrogen flow were denoted as PI-Fe-600, PI-Fe-800, PI-Fe-1000, PI-Fe-1200, PI-Fe-1400, and PI-Fe-1600, respectively, the same as the PI film.

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 (D/Max2500VB2+P/C, Rigaku, Japan) using Cu K α 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 θ 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 size and the distribution of particles in the carbon films were investigated by a Hitachi JEM-3010 transmission electron microscope (TEM).

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).

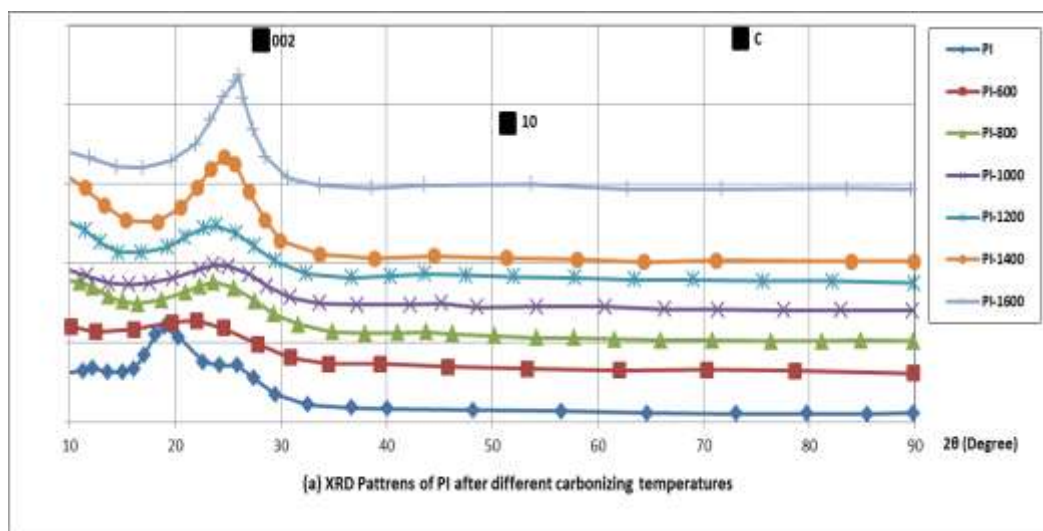
III. Result and Discussion

XRD measurement:

The effects of the carbonizing temperature on the crystal structures of carbon films derived from PI films, PI-Fe films were identified by XRD. Diffraction patterns for carbon films derived from pure polyimide film are shown in Figure no 2a. The pattern of PI has two small peaks at $2\theta=20.04^\circ$ and 25.38° , which indicates that PI film without carbonization has relatively low crystallinity. The 002 line of carbon films derived from polyimide film becomes sharper and moves to higher angles with increasing carbonizing 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 as the characteristics of graphite[20].

Figure no. 2b shows XRD patterns for PI-Fe films obtained at different carbonizing temperatures. Comparing these with PI film without carbonization, two characteristic peaks of the pure Fe_3O_4 sample at $2\theta=30.17^\circ$ and 35.60° corresponding to (220) and (311) Bragg reflection [17] can be observed in the PI-Fe film. With the carbonization temperature up to $800^\circ C$, only a very weak (400) reflection of pure Fe_3O_4 sample at 43.21° [17] can be detected in addition to the (002) reflection of graphite carbon. Most of the extra diffraction peaks supposed to be Fe_3O_4 and $\alpha-Fe$ appear when the sample is treated at $1000^\circ C$, implying the pyrolysis of Fe_3O_4 . After carbonization at $1400^\circ C$ and above, only two peaks at 44.85° and 54.08° could be assigned to the (110) reflection of hexagonal $\alpha-Fe$ and the (004) reflection of carbon[21], indicating that Fe_3O_4 has completely converted to $\alpha-Fe$ at temperatures higher than $1400^\circ C$. Meanwhile, the (002) diffraction peak in PI-Fe film at the same carbonization temperature is narrower and sharper than that of pure PI film, implying that Ferrum particles can facilitate the carbonization of matrix polyimide.



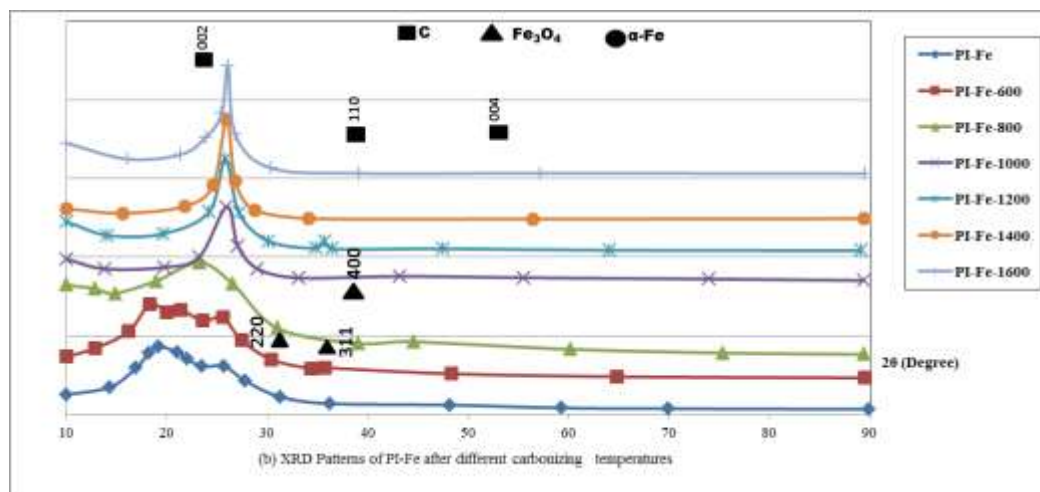


Figure no 2: XRD patterns of carbonized films; (a) PI, (b) PI-Fe with different carbonizing temperature

SEM and TEM of PI-Fe composite films with different carbonization temperatures

The surface of the films was observed by SEM. Figure no.3 shows the SEM images of the PI-Fe films treated by different carbonization temperatures. There are plenty of particles existing on the surface of the films, and the size of the particles becomes larger with increase of the carbonization temperature. The images a, b, and c also show the good dispersion and compatibility of Ferrum in polyimide matrix.

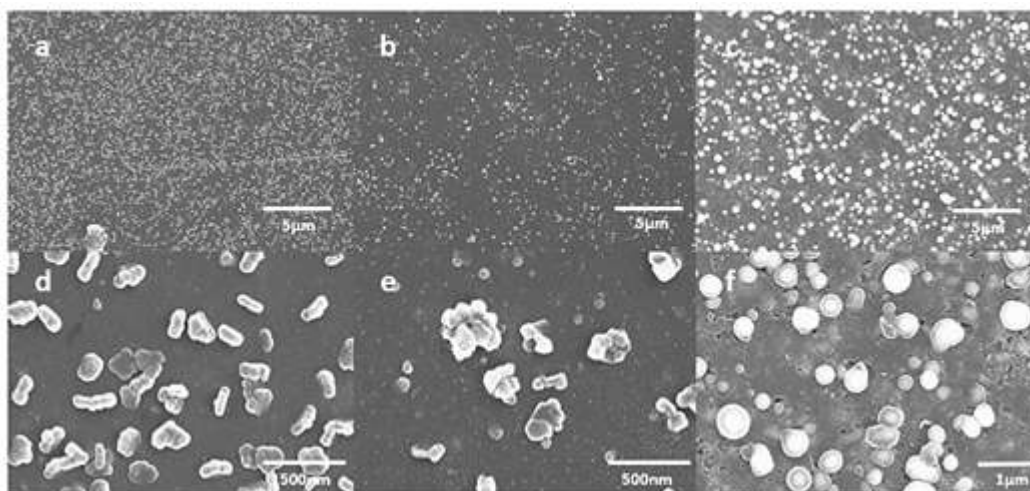


Figure no 3: SEM images of PI-Fe treated by different carbonization temperatures. (a) 600°C; (b) 800°C; (c) 1400°C; d, e, f are the high magnification images corresponding to a, b, c.

Figure no.4 describes the morphology of PI-Fe film treated by different carbonization temperatures. The Ferrum complex particles can be clearly seen. As panel b shows, the growth of particles can be negligible. However, as the carbonization temperature increases, the average size of Ferrum particles is about 100 nm in the film carbonized up to 1000°C. In the sample of PI-Fe-1200 film, the average size of particles increased to 170 nm. The present result shows that the growth of Ferrum clusters on carbon films with increase in carbonization temperature, which is consistent with the XRD result. When treated below 600°C, the alteration in the position and intensity of the peaks can be negligible. And the composite profile of the 002 diffraction line was also observed, a sharp peak being detected markedly with the increase of carbonization temperature. This result indicates that these particles become larger with the increase of carbonization temperature. So we can draw the conclusion that the crystallinity of the carbon materials can be enhanced due to the clustering of the Ferrum particles.

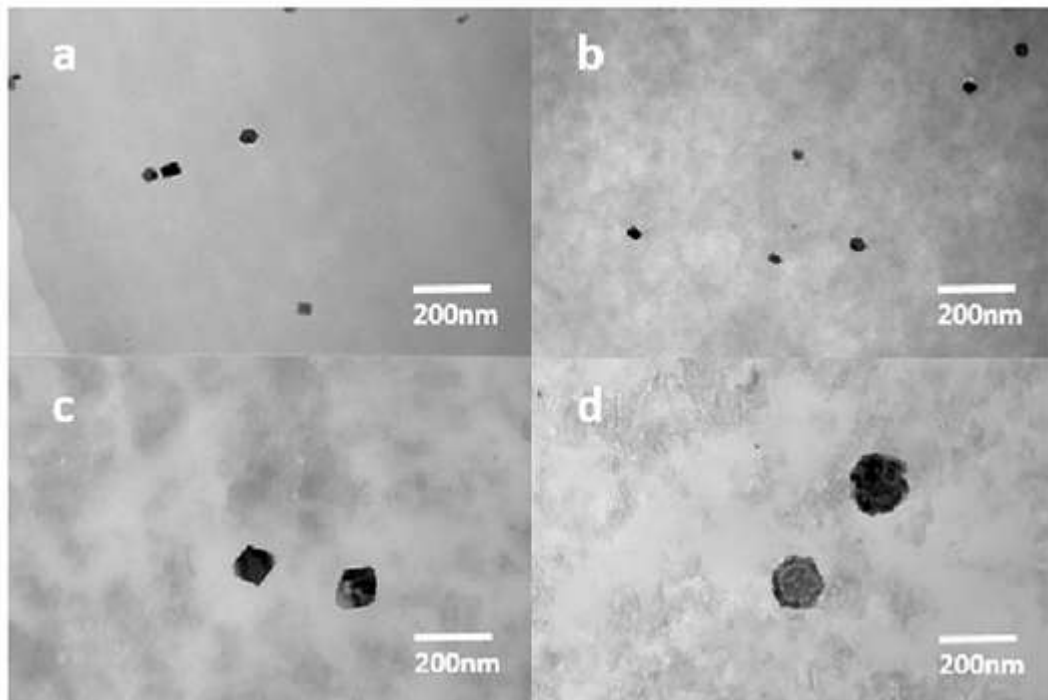


Figure no 4: Transmission electron micrographs of PI-Fe treated by different carbonization temperatures. (a)before carbonization; (b) 600°C; (c) 1000°C;(d) 1200°C.

Electrical conductivity:

The carbonized films were first tested for their electrical conductivity, and the variation trend of the series' surface resistivity depending on carbonization temperature is depicted in Figure no.5. At carbonization temperatures lower than 600°C, the sheet resistivities of all the carbon films are too high to be measured, which is caused by the high resistance of polyimide matrix. Above 800°C, the surface resistivities of all the carbonized films decrease with increase of the carbonization temperature, originating from the enhancement of crystallinity. In addition, the surface resistivities of all the carbon films containing Ferrum are 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 no. 1. This indicates that Ferrum have a catalytic effect on the carbonization of the composite films. At low carbonization temperatures, Ferrum and begin to be reduced which may play a key role in promoting the carbonization.

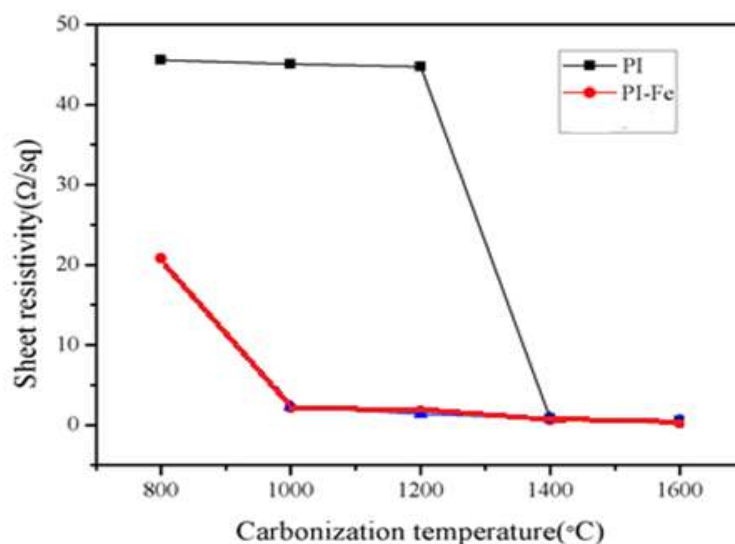


Figure no5: Variation of surface resistivity of carbonized films with carbonization temperatures

Table1 no 1: Sheet resistivity of carbonized films with different carbonization temperatures

Specimens	Sheet resistivity (Ω/sq)				
	800°C	1000°C	1200°C	1400°C	1600°C
PI	45.58	45.07	44.72	0.80	0.55
PI-Fe	20.80	2.20	1.80	0.63	0.23

Magnetic properties:

The magnetic behavior of PI, PI-Fe carbon films at different carbonization temperature is obvious from the magnetic hysteresis loops shown in Figure no.6(a, and b). In the magnetic hysteresis curves, the carbon films containing Ferrum displayed typical ferromagnetism with small coercivity and saturation magnetization. However, the curves of PI 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 the Table no.2. The magnetic properties of PI-Fe carbonized films can be adjusted by changing the carbonization temperature. With increase of the carbonization temperature, the M_s Values of the carbon films increased from 0.54592 emu/g to 1.7414 emu/g, and the coercive force decreased at the same time. This may be due to the fact that Ferrum complex particles become large with increase of the carbonization temperature.

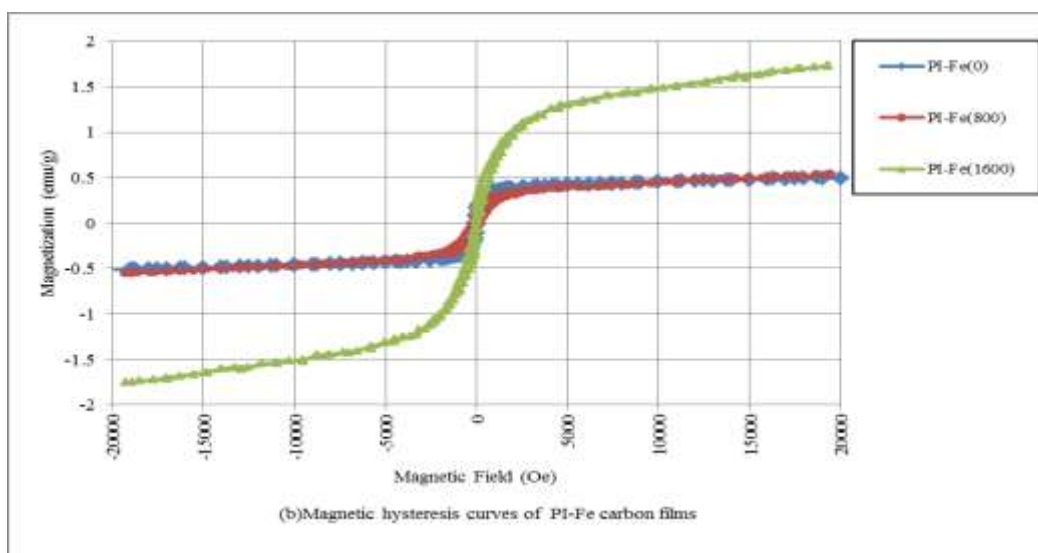
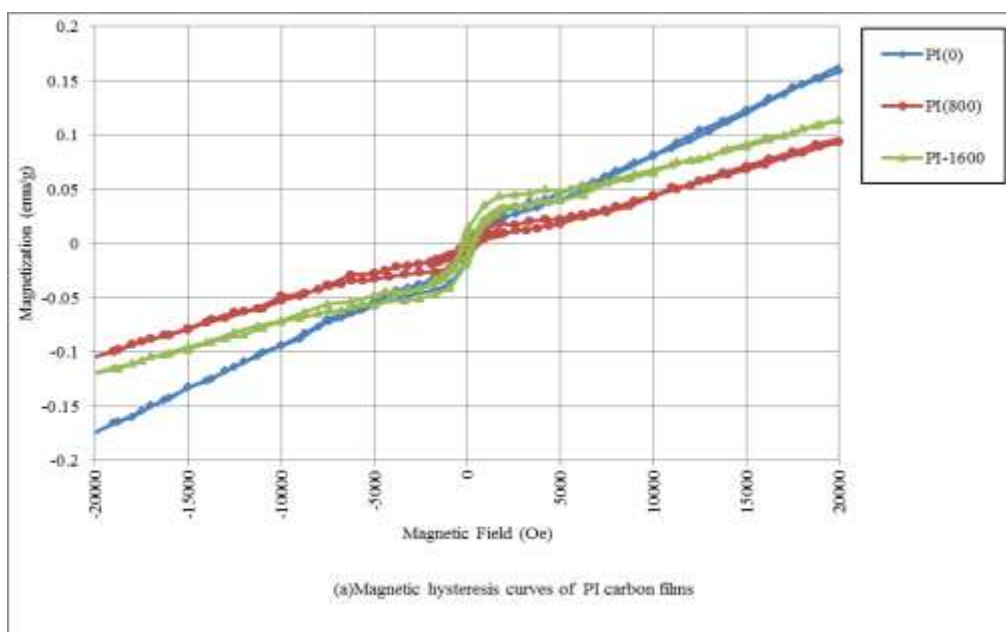


Figure no 6: Magnetic hysteresis curves of (a) PI, (b) PI-Fe carbon films

Table no 2: Magnetic properties of the carbon films

Sample	Ms (emu/g)	Mr (emu/g)	Hc (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-Fe	0.50979	0.094700	53.450
PI-Fe-800	0.54592	0.10887	167.18
PI-Fe-1600	1.7414	0.17797	141.79

IV. Conclusion

In this investigation, the effect of adding metal on electrical conductivity and metal particle growth in polyimide films and polyamide metal films after carbonization has been successfully studied. Carbonization was performed at temperatures between 600 ° C and 1600 ° C, and the results were well aligned with TEM notes on the same films. The study demonstrated the following:

- 1) Adding metal to a polyimide contributes to increasing electrical conductivity.
- 2) The effect of carbonization on conductivity is the same after carbonization is more than 1600 ° C, may this is due to an improvement in the balance in the carbon matrix crystal by forming pores in the film due to reduced pheromones.
- 3) In carbon films, the volume of metal particles grew from about 100 nanometers after 1,000 ° C to about 170 nanometers after 1400 ° C. As a result of particle growth, a transition from paramagnetic to ferromagnetic behavior was observed. This may be due to the fact that iron complex particles become larger with an increase of the carbonization temperature.

References

- [1]. Silcox R. Development of polyimide foam for aircraft sidewall applications. 51st AIAA Aerospace Sciences Meeting Including the New Horizons Forum and Aerospace Exposition, 2013.
- [2]. Weiser E S, Johnson T F, Clair T L S, et al. Polyimide foams for aerospace vehicles. *Highperformancepolymers*, 2000, 12(1): 1-12.
- [3]. Tang Q Y, Chan Y C, Wong N B. Investigation of polyimide/carbon nanotube nanocomposites for high temperature electronic packaging applications. *Proceedings-2009 IMAPS International Conference on High Temperature Electronics Network*, 2009: 110-115.
- [4]. An H Y, Zhan M S, Wang K. Synthesis and properties of fluorene-based polyimide adhesives. *Polymer Engineering & Science*, 2011, 51(8): 1533-1540.
- [5]. Li Y, Fu S Y, Li Y Q, et al. Improvements in transmittance, mechanical properties and thermal stability of silica-polyimide composite films by a novel sol-gel route. *Composites Science & Technology*, 2007, 67(11): 2408-2416.
- [6]. Saeed M B, Zhan M S. Adhesive strength of nano-size particles filled thermoplastic polyimides. Part-I: Multi-walled carbon nanotubes (MWNT)-polyimide composite films. *International Journal of Adhesion & Adhesives*, 2007, 27(4): 306-318.
- [7]. Xu L, Chen G, Wang W, et al. A facile assembly of polyimide/graphene core-shell structured nanocomposites with both high electrical and thermal conductivities. *Composites: Part A-Applied Science and Manufacturing*, 2016, 84:472-481.
- [8]. Burger A, Fitzer E, Heym M, et al. Polyimides as precursors for artificial carbon. *Carbon*, 1975, 13(3):149-157.
- [9]. Doyama M, Ichida A, Inoue Y, et al. Partial carbonization of aromatic polyimide films. *International Journal of Inorganic Materials*, 2001, 3(8): 1105-1107.
- [10]. Inagaki M, Meng L J, Ibuki T, et al. Carbonization and graphitization of polyimide film“Novax”. *Carbon*, 1991, 29(8): 1239-1243.
- [11]. Doyama M, Ichida A, Inoue Y, et al. Electrical properties of amorphous carbon films. *ScriptaMaterialia*, 2001, 44(8): 1191-1194.
- [12]. Sharma A, Saito I, Nakagawa H, et al. Effect of carbonization temperature on the nickel crystallite size of a Ni/C catalyst for catalytic hydrothermal gasification of organic complexes. *Fuel*, 2007, 86(7-8):915-920.
- [13]. Kaburagi Y, Toriyama T, Yoshida A, et al. Carbonization behavior of polyimide film containing iron complex in relation to magnetic properties. *Journal of Materials Research*, 2001, 16(02): 352-365.
- [14]. Sode K, Tanaka M, Suzuki Y, et al. Nickel nanoparticle chains inside carbonized polymer nanofibers: Preparation by electrospinning and ion-beam irradiation. *Nanoscale*, 2013, 5(17): 8235-8241.
- [15]. Zhu J, Wei S, Dan R, et al. Magnetic polyacrylonitrile-Fe@FeO nanocomposite fibers-Electrospinning, stabilization and carbonization. *Polymer*, 2011, 52(13): 2947-2955.
- [16]. Bin Y, Oishi K, Ai K, et al. Catalytic effect of nickel under carbonization of polyimide films. *Carbon*, 2005, 43(8): 1617-1627.
- [17]. Zhou H, Yu W, Qu C, et al. Facile one-step synthesis of PI/Fe₃O₄ composite microspheres from poly(amic acid) triethylamine salts and Fe(III) ion. *Journal of Materials Science: Materials in Electronics*, 2015, 26(12): 9789-9794.
- [18]. Oka H, Inagaki M, Kaburagi Y, et al. Incorporation of iron particles into carbon films derived from polyimide. *Solid State Ionics*, 1999, 121(s 1-4): 157-163.
- [19]. Inagaki M, Ohta N, Hishiyama Y. Aromatic polyimides as carbon precursors. *Carbon*, 2013, 61(11): 1-21.
- [20]. Su J, Lua A C. Influence of carbonisation parameters on the transport properties of carbon membranes by statistical analysis. *Journal of Membrane Science*, 2006, 278(s 1-2): 335-343.
- [21]. Kaburagi Y, Hishiyama Y, Oka H, et al. Growth of iron clusters and change of magnetic property with carbonization of aromatic polyimide film containing iron complex. *Carbon*, 2001, 39(4): 593-603.

Fathi Etaher Elbakoush, et. al. “Effect of Ferrous metal on The Electrical Conductivity and Growth of Metal Particles after Carbonization for Polyimide Films.” *IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE)*, 17(4), 2020, pp. 45-51.