Synthesis and Characterization of Magnetic Iron-Modified Polyimide Films

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The most common method of preparing magnetic tapes and disks is to coat a polymer substrate with a slurry of magnetic oxide and binder. Typically the magnetic material has been either γ-Fe_2O_3 or Fe_3O_4.[1] An alternative route to preparing magnetic polymeric media is to synthesize the magnetic material in situ when preparing the polymeric substrate.[2] An in situ synthesis can be performed in one of two ways. The first consists of thermally decomposing a metal complex, contained in the polymer film, to its corresponding oxide while curing or drying the film. The second consists of infusing additional reactants from solution into the polymer to transform an encapsulated metal complex to its corresponding oxide. Typically, the second method emulates known solution reactions for the synthesis of specific metal oxides.

We report in this communication that films cast from viscous poly(amide acid) solutions, containing up to 4.2 wt % $Fe(acac)_3$, form free-standing magnetic polyimide films containing highly dispersed iron oxide particles upon thermal imidization.

The monomers used in this study were 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) and 4,4'-oxydianiline (ODA). Poly(amide acid) solutions were synthesized by reacting 4.0 mmol of each monomer in dry N,N-dimethylacetamide (DMAc); the resulting solution was stirred for 2 h. Four iron(III) acetylacetonate, $Fe(acac)_3$, modified solutions were prepared by the addition of 0.5–2.0 mmol of $Fe(acac)_3$ to the poly(amide acid) solution. The iron poly(amide acid) solution was then stirred for an additional 2 h. All of the $Fe(acac)_3$/poly(amide acid) solutions contained 14% solids on a monomer, dopant, and solvent basis. Films were prepared by casting the viscous solution at 0.020 in. onto a glass plate via a doctor blade, followed by thermal imidization at 80 °C for 20 min and 100, 200, and 300 °C each for 1 h under an atmosphere of dry air. The side of the film exposed to the curing atmosphere is referred to as the air side. Likewise, the side of the film exposed to the glass plate is referred to as the glass side. The fully cured iron-modified films contained a maximum of 5.13 wt % iron.

Poly(amide acid)/$Fe(acac)_3$ solutions containing several concentrations of $Fe(acac)_3$ (Table I) were cast as films that were dark red prior to curing. Smooth free-standing red-brown films were obtained following thermal imidization. Films 1 and 2 were flexible; however, however films 3 and 4 were very brittle (Table II). Elemental analysis[3] of the films reveals that less than 5% of iron is lost during the curing process. When $Fe(acac)_3$ is heated in a thermal balance under the same conditions (i.e., time, temperature, and atmosphere) as the modified films are during their curing process, a weight loss of 2–6% due to sublimation is observed. In constrast, we find that when iron carbonyls are used as the dopant material, nearly all the iron carbonyl is lost during the curing process.

(1) *Magnetic Recording*; Lowman, E. E., Ed.; McGraw-Hill: New York, 1972; pp 45–61.

(2) Calvert, P.; Mana, S. *J. Mater. Sci.* **1988**, *23*, 3801.

(3) Elemental analyses were performed in our laboratory by decomposing the iron-modified film at 500 °C in air followed by acid digestion. Percent iron was determined by atomic absorption spectroscopy.

Table I. Concentration of Iron in the Modified Polyimide Films

film	wt % of Fe prior to curing[a]	wt % of Fe in final film[b,3] actual	theoret
1	0.171	1.35	1.41
2	0.313	2.64	2.76
3	0.429	4.00	4.06
4	0.524	5.13	5.31

[a] Determined on a monomer, solvent, and dopant basis. [b] Determined on a polyimide and Fe_2O_3 basis, assuming no residual DMAc or acac ligand.

Table II. Physical Properties of the Iron-Modified Polyimide Films

film	PDT[a] air	N_2	condition[b]
blank	593	628	flexible
1	418	528	flexible
2	421	526	flexible
3	419	508	brittle
4	413	505	brittle

[a] Polymer decomposition temperature, PDT, is the temperature at which 10 wt % of the polymer is lost. [b] A film that can be folded onto itself without fracturing is considered flexible; films that do not pass this test are termed brittle.
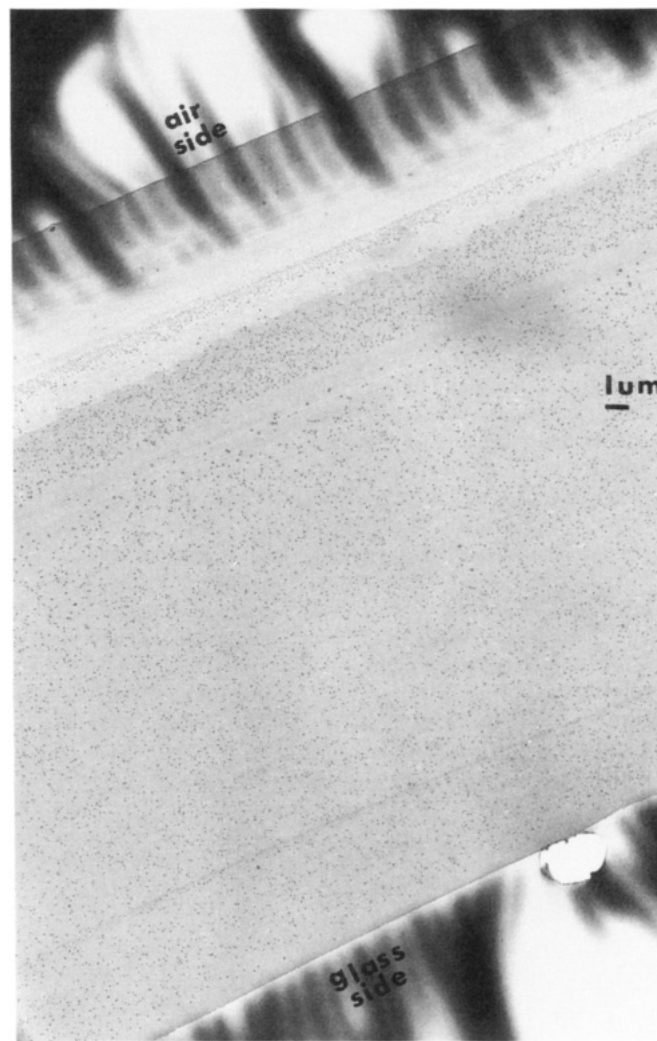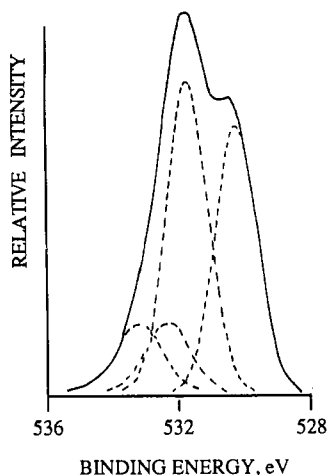

Figure 1. Transmission electron micrograph of film 3. The dark lines perpendicular to both surfaces are a result of ultramicrotoming a very brittle film.

Figure 1 shows a transmission electron micrograph (TEM) of film 2. Similar micrographs were obtained for

Figure 2. Oxygen (1s) photopeak of film 4 (—), along with the best curve fit (---).

the other three films. The most striking feature in this micrograph is the formation of highly dispersed particles in the polymer matrix. Furthermore, these particles have a near uniform size distribution. The average particle size, in this micrograph as well as the other three, ranged between 20 and 80 nm. Also present in the TEMs is a depletion zone of 4.6 μm. The loss of 5% of the dopant material alone cannot account for this depletion zone. Therefore this material is believed to have either formed atomically dispersed particulate matter that cannot be observed by TEM or has migrated from this area of the film. Upon examination of higher magnification TEM photos, it is difficult to distinguish phase contrast from surface and near-surface particulate matter. X-ray photoelectron spectroscopy (XPS) revealed evidence of a surface layer of iron oxide (vida infra) on the modified films. Up to 10 atom % iron was observed in the first 50 Å of the air-side surface. Thus supporting the theory of atomically dispersed particulate matter.

Figure 2 shows a typical oxygen(1s) photopeak obtained from the analysis of the iron-modified films. The top spectrum was generated from film 4. The curve fit of this spectrum is represented by the set of four bands shown as the bottom spectrum. Bands at 533.2, 532.3, and 531.6 eV[4] are assigned to the ether, ketone, and imide functionalities of the polyimide.[5] These oxygen functionalities have a relative concentration of 1:1:4, which is what is expected for a BTDA/ODA polyimide. The peak at 530.1 eV is assigned to an oxide oxygen. Similar binding energies have been reported for oxygen in various iron oxides.[6] The relative atomic concentrations of oxygen to iron in the four films ranged between 1.34 and 1.70, which corresponds to a stoichiometry of either Fe_2O_3 or Fe_3O_4. The position and width of the iron(2p) photopeak was found to be independent of the oxidation state of the iron in model iron oxides.

X-ray powder diffraction was used to aid in the identification of the iron oxide contained in the polyimide matrix. Of the four films, only film 4 gave a substantial signal in the X-ray diffractogram. The two major reflections in the spectrum were at *d* spacings of 2.52 and 1.48 Å, which are indicative of either γ-Fe_2O_3 or Fe_3O_4. The reflections used to confidently distinguish the two oxides,

as determined from authentic samples, were not observed in our samples due to the substantial background noise arising from the polymer matrix. However, it was observed from the X-ray diffraction pattern that reflections due to FeO, α-Fe_2O_3, or any iron oxyhydroxides were not present.

Magnetic measurements performed on the iron-modified films further suggest the transformation of the $Fe(acac)_3$ dopant to γ-Fe_2O_3 or Fe_3O_4. The coercivities of the iron-modified films were between 105 and 130 Oe. These values are lower than most literature values for iron oxides used in magnetic applications; however, the iron oxide particles in our films were cubic while higher coercivities are indicative of needlelike particles.[7]

We also find that heating only $Fe(acac)_3$ to 300 °C in a dry air atmosphere produces γ-Fe_2O_3 as determined by X-ray diffraction. Furthermore, thermal treatment of Fe_3O_4 at 300 °C in dry air for 1 h also produces γ-Fe_2O_3. Therefore if Fe_3O_4 was produced in the films it would readily be transformed to γ-Fe_2O_3 during the last stage of the thermal imidization process. For these reasons it is believed that the iron oxide particles produced in the films are γ-Fe_2O_3.

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Intercalation Chemistry of Layered FePS₃. An Approach toward Insulating Magnets below 90 K

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In recent years, considerable effort has been devoted to the synthesis of insulating, molecular-based materials exhibiting bulk ferro- or ferrimagnetism. However, most materials synthesized so far have very low Curie temperatures, typically in the range 1–15 K.[1,2] Very few exceptions occur, such as ammonium tetrachlorochromate(II), which orders ferromagnetically in the range 50–60 K.[1] This report describes a semiconducting intercalate in the $FePS_3$ family, namely, $Fe_{1-x}PS_3(pyridinium)_{2x}(solv)_y$ ($x \approx 0.12$), which exhibits spontaneous magnetization below $\approx$90 K.

Transition-metal hexathiohypodiphosphates MPS_3, where M stands for a metal in the II+ oxidation state, form a family of lamellar materials, often described as broad-band semiconductors,[3] structurally similar to the well-known lamellar dichalcogenides (for a review see the article by Brec[4]). Several MPS_3 compounds display a unique

(4) All photopeaks were referenced to the carbon (1s) peak at 284.6 eV, of the aromatic groups in the polymer backbone.
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(2) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* **1988**, *21*, 114 and references therein.
(3) Klingen, W.; Ott, R.; Hahn, H. *Z. Anorg. Allg. Chem.* **1973**, *396*, 271.
(4) Brec, R. *Solid State Ionics* **1986**, *22*, 3 and references therein.