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Magnetic alignment of particles in composite films

E. BREVAL, M. KLIMKIEWICZ, Y. T. SHI, D. ARAKAKI, J. P. DOUGHERTY
Materials Research Laboratory, Materials Research Institute, Penn State University, University Park, PA 16802, USA
E-mail: EXB6@psu.edu

Films with anisotropic electric properties were created by a processing technique that produces an alignment of μm sized iron particles in a polymer film. The magnetic aligning process was observed to create a formation of iron particle columns parallel to the aligning magnetic field. The degree of alignment can be quantified by measurements of the electrical impedance.

1. Introduction

Modern electronic packaging requirements often include customized dielectric or conductive layers which serve as specialized interconnects between circuit components or even as embedded passive components [1]. This is why there is a growing need for thick films with tailorable electrical properties. For example, a 0–3 ceramic-polymer composite was developed for ultrasonic medical transducers [2]. Composites with aligned $BaTiO_3$ particles were prepared to create anisotropic dielectric properties for capacitors [3]. Anisotropic conductive films are currently used to mount high interconnect density packages [4].

The objectives of this study are: (a) to prepare films with anisotropic electrical properties by an alignment of particles in a polymer film and (b) to examine the nature of this alignment. This includes the role of the crystallographic orientation of the individual particles, and the rearrangement of particles into columns. In addition, the role of the orientation of possible domains or sub grains within one particle was explored. Using the mixing rules it is possible to predict the electrical properties when dispersing conducting particles within a dielectric matrix [4–6].

Particles in a polymer matrix can be aligned either in an electric or a magnetic field. Magnetic alignment requires a much simpler experimental set-up than electrophoretic or dielectrophoretic alignment. The experiments in this study are focused on the magnetic alignment of iron particles in a polymer. The reason for choosing iron particles is that this material aligns itself within a magnetic field, but has negligible residual magnetization. This allows enhanced dispersion in a fluid medium contrary to materials such as Fe_3O_4, which have a significant residual magnetization [6].

The model used in the present investigation is an analogue between a particle arrangement and an electrical circuit analogue [7]. Parameters are (1) the resistance (R) of the particles, (2) the capacitance (C) of the polymer gap, the distance (D) between columns of particles, and the distance (d) between particles in a column. See Fig. 1 in which also the directions x, y, and z are shown. This paper will demonstrate different types of magnetic alignments of iron particles in a polymer film that are possible. It will describe the film by quantifying the alignment in terms of (a) crystallographic orientation of the particles, (b) distribution of the particles in the film (random or in columns), and (c) electrical impedance.

2. Experimental procedure

2.1. Preparation of films on brass substrates

Brass plates, 0.4 mm thick were used as substrates. The film consisted of iron particles (Fe (1–3 μm, Alfa Aesar) and alumina particles 0.05 μm (Buehler) in a polymer (polyimide (PI2808, Dupont) or polysulfone (Alpha Metals). An adhesion promoter (T2507, United Chemical Technologies) was used on the substrates. The particles and the polymer were mixed using ultrasonic homogenization.

Samples were prepared using 18 to 30 wt% iron in the polymer matrix. The adhesion promoter was first applied to the cleaned brass using a spin-coater running at a speed of ~25 rpm. The substrate was heated by an infrared lamp (substrate surface temperature 130°C) for 5 minutes. After cooling, the paste was spun on the substrate at a speed of 1500 rpm. Selected pairs of specimens were cured inside a furnace either with no magnetic field or in a magnetic field created by the fixture shown in Fig. 2. The curing was performed by heating from room temperature at a rate of 3°C/min., holding at 180°C for 6 hours followed by cooling at the furnace rate. The cured films were 140 ± 10 μm thick.

2.2. Magnetic alignment

The equipment for the alignment of iron particles in a magnetic field is shown in Fig. 2. The set-up for vertical alignment produced a B-field of 300 to 400 Gauss and that of the horizontal alignment produced 400 Gauss. The permanent magnets were ferrites, which can easily

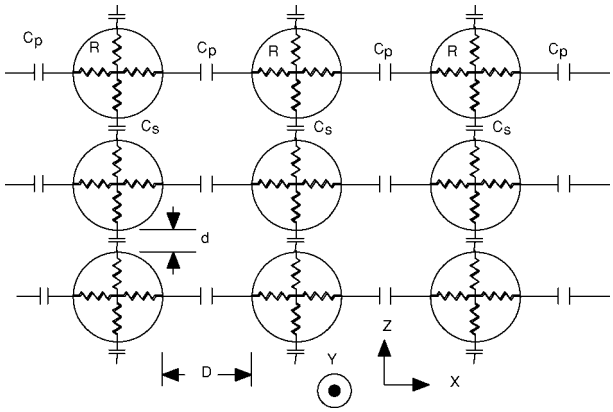

Figure 1 Model of the particle arrangement and the electrical circuit analogue. *R* is the resistance of a particle, *C* is the capacitance of the polymer gap. *D* is the distance between columns of particles, *d* is the distance between particles in a column. The directions *x*, *y*, and *z* are shown.

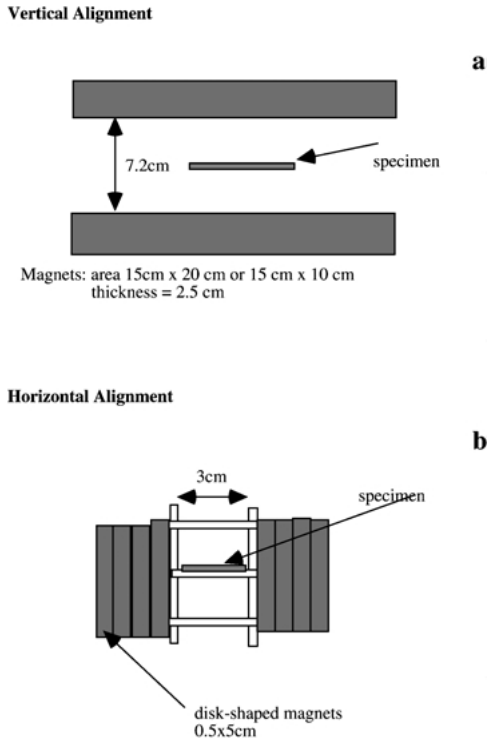

Figure 2 Fixtures for alignment of iron particles between permanent magnets.

maintain magnetism up to at least 200°C without irreversible damage.

2.3. Optical microscopy

A transmitted light optical microscope was used to observe iron particles during increasing magnetic fields. Iron particles were dispersed in a transparent liquid as a thin slurry on a glass slide. The individual particles were observed at $\sim 500\times$. The arrangement is shown in Fig. 3. The suspension on the glass slide was observed while two sets of magnets were placed approximately 50 cm on each side of the suspension on the glass slide and then brought slowly together towards the slide to increase the magnetic field. This experiment was performed several times. A new mixture of slurry was used for each trial in order to be able to observe the alignment process of randomized particle distributions.

2.4. X-ray diffraction

X-ray diffractometry was carried out using an automated X-Ray Powder diffractometer PAD V, Scintag, Santa Clara, CA using Cu K_α radiation and $\lambda = 1.540598$ Å. Slow scans of 1° per minute were obtained. The intensities of the *hkl* reflections were calculated on the Scintag computer as areas of background subtracted $K\alpha_2$ stripped peaks. A selected aligned sample containing only polyimide and iron powder was used for the X-Ray tests. The iron powder (1–3 μm), a glass plate, a glass plate with cured polyimide without particles, and an uncoated brass substrate were used as standards. A preferred orientation of a crystalline phase was investigated by measuring the *hkl* intensities and comparing them to the corresponding intensities of a randomly oriented standard [8].

2.5. Scanning electron microscopy

A Hitachi S-3500N Scanning Electron Microscope (SEM) was used to image some of the film cross-sections. The electron beam can penetrate through several μm of polymer, which is very useful for evaluating the position of iron particles below the surface. High atomic number iron particles show up very bright on Backscatter Electron micrographs, whereas the low atomic number alumina and polymer appear darker. An Electroscan Environmental Scanning Electron Microscope (ESEM) E-3 was used for the study of some of the aligned films. The ESEM does not require a conducting coating on non-conductive specimens, and therefore polyimide can easily be studied. This makes imaging of uncoated films easier than in some conventional SEMs. The films were observed either on the as-is film surface as a top view, or on a polished cross section.

2.6. Transmission electron microscopy

A Philips 420 EM was used at an acceleration voltage of 120 kV. A slurry of iron particles in isopropanol was transferred to a TEM grid followed by drying. Selected area electron diffraction patterns were obtained to identify the iron particles. Bright field (BF) and dark field (DF) images were obtained.

2.7. Impedance measurements

The brass substrate acted as a bottom electrode. Three to four top electrodes were made using conductive epoxy spots of about 2 mm diameter on the surface of the films. An HP 4263B LCR meter was used for determination of Impedance (Z), Phase Angle (Θ), Capacitance (C_p) and tan ∂ at 100 Hz, 1 kHz, and 100 kHz.

3. Results and discussion

3.1. Structural characterization

When the magnetic field was low (<100 Gauss) all iron particles showed a random distribution in the liquid on the glass slide when observed in the optical microscope. Increasing the magnetic field caused more

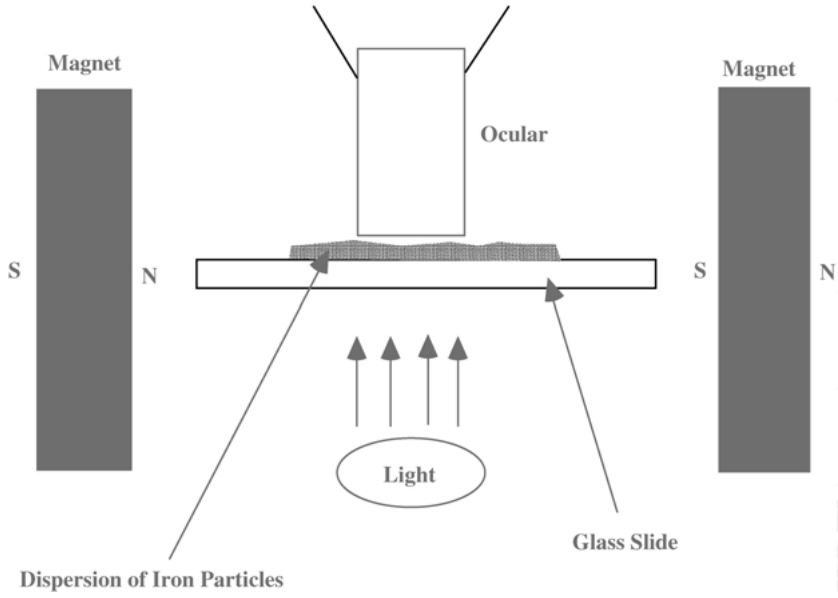

Figure 3 Sketch of optical microscopy experiment to observe alignment of iron particles dispersed in a fluid.

and more particles to join together and form longer and longer rows. Individual particles needed a stronger field to join a row than a cluster in which the particles already were close to each other. Individual particles located at a significant distance from clusters were carefully observed during the increase of the magnetic field to above 100 Gauss. As expected, elongated particles rotated to align lengthwise with the magnetic field, whereas it was not possible to detect any rotation of spherical particles. Careful inspection of many equi-axed particles revealed that it was possible to find some particles that were not completely spherical. As expected, such particles did not rotate while increasing the magnetic field because of negligible residual magnetization.

X-ray diffraction showed that the brass plate gave *d*-values as stated for synthetic brass in JCPDS 25-322 (Cu, Zn). The glass plate, and the glass plate with cured polyimide both gave no reflections at all. The powdered iron (1–3 μm) gave clear Fe lines (JCPDS 6-696, α iron, bcc). The Fe peaks were broadened to some degree; probably because of the small particle size. X-ray diffraction patterns of the final film showed only reflections from the brass plate and from the iron particles. The intensities of the iron peaks, calculated as peak areas (see Table I), were normalized to the strongest iron peak (110). The peak intensities indicate that there is no crystallographic preferred orientation of the iron particles in the films. This is in agreement with the observation that iron particles do not rotate when placed in a magnetic field.

TABLE I *hkl* Fe peak intensities of films (30 wt% Fe in polyimide) as compared to JCPDS intensities of Fe

	hkl				
Specimen	110	200	211	220	310
Unaligned	100	10.8	22.0	8.6	9.0
Vertically aligned	100	10.5	21.3	10.0	9.2
Horizontally aligned	100	13.2	19.6	10.3	9.1
JCPDS 6-696	100	20	30	10	12

All prepared films, with and without magnetic alignment, were studied in the SEM and ESEM. Fig. 4, a view of the surface of a prepared film, shows the uniform, but random distribution of iron particles in the unaligned film sample. Figs 5 and 6, also surface views, show that in a magnetic field there is a clear arrangement

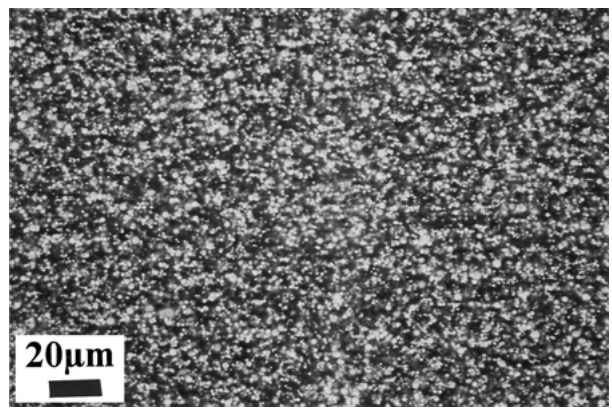

Figure 4 ESEM top view micrograph of an unaligned composite film showing random distribution of 1–3 μm iron particles in a polymer.

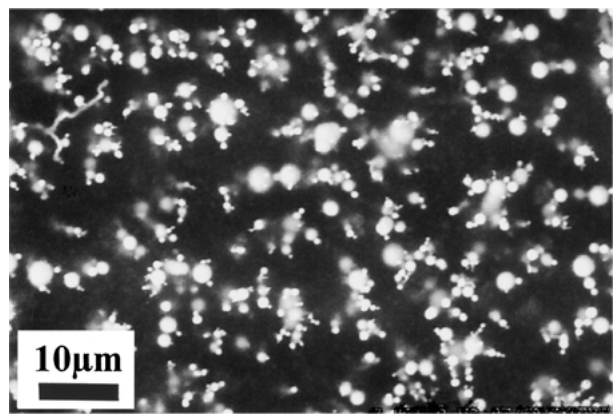

Figure 5 SEM BSE top view micrograph of a composite film consisting of 1–3 μm iron particles in a polymer. It is aligned in rows parallel to a magnetic field of 400 Gauss perpendicular to the film plane. The iron particles appear bright. The clustering is a result of the vertical alignment.

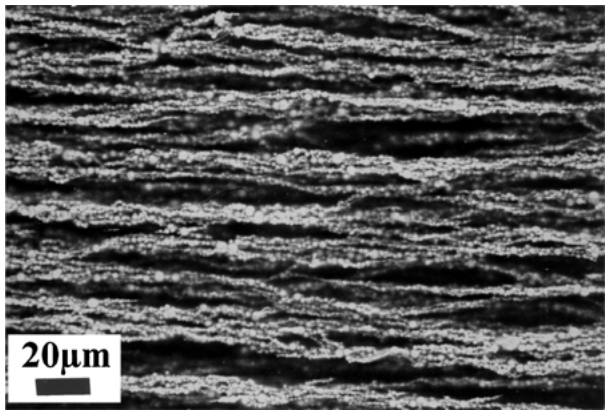

Figure 6 ESEM top view micrograph of a composite film consisting of 1–3 μm iron particles in a polymer. It is aligned in rows parallel to a magnetic field of 400 Gauss parallel to the film plane.

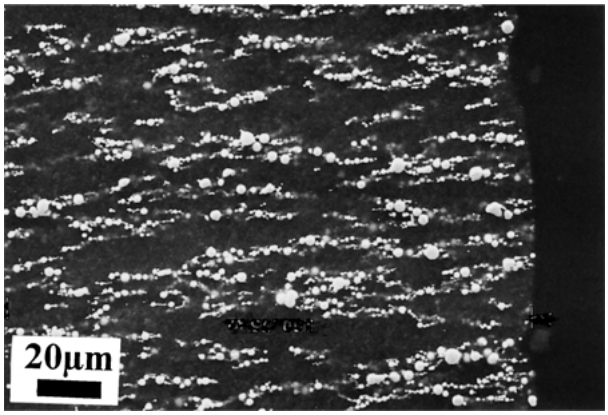

Figure 7 SEM BSE micrograph of a cross-section of a composite film, aligned in a magnetic field of 400 Gauss perpendicular to the film plane. The iron particles appear bright. The iron columns are parallel to the aligning magnetic field.

of iron particles in columns parallel to the magnetic field. In Fig. 5 the magnetic field is perpendicular to the film (vertical); the clustering is a result of the vertical alignment. In Fig. 6, the field is parallel to the film (horizontal); the image clearly shows the alignment.

Selected samples were cut, and cross sections polished for the observation of iron particle configuration. Iron columns arranged by a vertical magnetic field are shown in Fig. 7.

TEM investigations showed that each iron particle consisted of one single crystal. Dark field images were obtained using several reflections, but domains or sub grains within an individual particle were not detected. See Fig. 8 for (BF) and (DF) images.

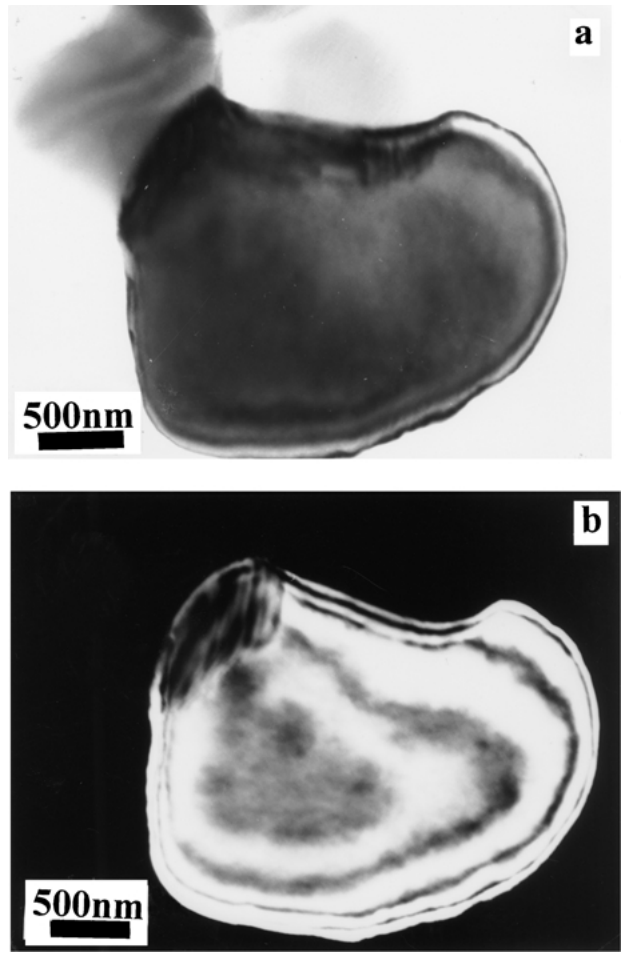

Figure 8 TEM micrographs of a typical 1–3 μm iron particle. BF (a) and DF (b) images show that each iron particle consists of one single grain with no sub grains or domains.

3.2. Electrical characterization

The capacitance (C_p) and tan ∂ were measured on the three to four separated conductive spots on each sample. The standard deviation was 1 to 10%, and the average values were used for calculation of the anisotropy. All of the unaligned samples were electrical insulators. The small capacitance and low tan ∂ numbers (Table II) for the 100 kHz data indicate that the composites consist of unconnected iron particles or clusters

TABLE II Impedance measurements of films containing 25 wt% Fe and 5 wt% Al_2O_3 in polyimide using a test voltage of 1 V·rms and varying frequencies

Alignment	Frequency (kHz)	$\lvert Z\rvert$ (Ω)	Θ (degrees)	C_p (F)	tan ∂	Anisotropy (Z_{none}/Z_{vert})
None	0.1	2.9 MΩ	−9.1	0.09nF	nd	
None	1	1.4 MΩ	−4.4	71.5pF	1.0	
None	100	3.1 kΩ	−81.3	50.7pF	0.15	
Vertical	0.1	265 Ω	−0.01	1.0nF	nd	10943
Vertical	1	264 Ω	−0.02	300pF	nd	5303
Vertical	100	260 Ω	−3.0	180pF	nd	11.9
Horizontal	0.1	108 MΩ	−90.7	13pF	0.0001	
Horizontal	1	11.3 MΩ	−89	14.3pF	0.01	
Horizontal	100	121 kΩ	−88	13.7pF	0.03	

Results outside the range of the meter is marked with nd. The anisotropies are calculated as Z_{none}/Z_{vert}.

(0–3 connectivity) in an insulating matrix [9]. The effects of the magnetic alignment can be clearly seen, since the phase angle of the electrical impedance goes from approximately -90° (a pure capacitor) for horizontal alignment to close to zero (a pure resistor) for vertical alignment. The unaligned samples have impedance magnitude, phase angle, capacitance and $\tan\partial$ values in between those of the vertically and horizontally aligned samples. The anisotropies were calculated as the ratio between the impedances of the unaligned and the aligned samples. As expected the anisotropies decrease with increasing frequencies, since there is less contribution from interfacial conductivity, which freezes out at higher frequencies. The low phase angle for the 0.1 and 1 kHz electrical impedance measurements suggests that the insulating region between particles is very small [10]. The particle to particle proximity puts the composite near the critical point for percolation, the volume fraction of conductor for which the composite rapidly decreases in electrical conductivity from an insulator to a conductor.

The arrangement of particles lined up in rows in an aligned film fits a series model for each column as shown in Fig. 1. The iron particles are modeled as a pure resistance, R, and the insulating gaps between particles are modeled as pure capacitors (C_p and C_s). The capacitance between particles is inversely proportional to the spacing. Therefore, since $D \gg d$ for aligned films the impedance in the z direction (series) is expected to be lower than the impedance in the x-y direction (parallel). The C_p is smaller ($C \propto 1/d$) than the C_s along the columns.

The electrical impedance of the composite can be modeled by making several simplifying assumptions. First it is assumed that the iron particles are cubes, 2 μm on an edge. For the 21 volume percent loading it can be estimated that for the 140 μm thick film 83 μm is iron (42 particles) and 42 μm inter-particle polymer. Using a parallel plate capacitor model would predict a capacitance for our samples of about 1.8 pF. This is much lower than the 50 pF measured for the unaligned samples.

Clearly the composite is close to the percolation limit predicted for conductor-epoxy composites so a simple series model is not accurate [11, 12]. Applying General Effective Media theory is beyond the scope of this paper. However, as long as the composite is acting like an insulator we can approximate the 3-3, three-dimensional permittivity of the composite using the logarithmic mixing rule given by Kingery [6]:

$$\log K = V_m \log K_m + V_p \log K_p$$

where K is the effective relative dielectric constant of the composite, V_m and V_p are the relative volume percent of the matrix phase and particle phase respectivily, and K_m and K_p are the relative dielectric constants of the matrix phase and particle phase respectivily.

In the present case the insulating and low dielectric constant matrix phase is composed of 89% polyimide and 11% aluminum oxide with dielectric constants of 3.2 and 10 respectively. Using the logarithmic mixing rule predicts a dielectric constant of 3.63 for the matrix.

The capacitance of the iron-matrix composite can be estimated by assuming that the metallic phase has a very high permittivity (10^9), which is consistent with the ratii of the relative conductivity of the two phases. The logarithmic mixing rule predicts an effective dielectric constant of about 215 for the composite, which corresponds to a capacitance of 43 pF for the present sample geometry.

The arrangement of particles in rows in an aligned film fits the model as shown in Fig. 1. The impedance in the z direction is lower than the impedance in the x-y direction because the C gap is higher ($C \propto 1/d$) than the C between the columns (because $D \gg d$). The present results therefore show that good electrical anisotropy can be achieved even when the horizontal alignment is not optimal, e.g., when the iron particles are not aligned completely perpendicular to the surface (Fig. 7).

4. Conclusions

A thick film containing micron sized iron particles dispersed in a polymer matrix has been made electrically anisotropic. This was accomplished by aligning the iron particles in the still wet film in the direction of a magnetic field and curing the polymer while still aligned. The individual iron particles line up in columns separated from each other; but the individual particles keep their random crystallographic orientation. The anisotropy can be characterized by impedance measurements perpendicular to the film.

Acknowledgement

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