Time dependence of magnetic moment of strontium-ferrite powder measured with a biaxial vibrating sample magnetometer (VSM)

Tanjina Nasreen Ahmed[1], Maria Camila Belduque[2], Binod D.C.[1], Jitendra S. Tate[1,2], and Wilhelmus J. Geerts[1,3]

1. Materials Science, Engineering, and Commercialization, Texas State University, 601 University Drive, San Marcos, TX 78666, USA
2. Mechanical and Manufacturing Engineering, Texas State University, 601 University Drive, San Marcos, TX 78666, USA
3. Department of Physics, Texas State University, 601 University Drive, San Marcos, TX 78666, USA

ABSTRACT

The magnetic hysteresis and viscosity of $SrO(Fe_2O_3)_6$/PA-12 filaments with 5wt% and 26wt% was determined with a biaxial VSM. The hysteresis curves indicate that manufactured samples have a flow induced anisotropy with an easy plane perpendicular to the filament's cylindrical axis. The M_x and M_y magnetic viscosity signals vary with field and field angle. The M_x magnetic viscosity is maximum in the easy plane and decreases to a factor of two along the macroscopic hard axis of the filament. The M_y magnetic viscosity is nearly zero along the hard axis and in the easy plane and is maximum for intermediate field angles.

INTRODUCTION

Polymer composites with magnetic particles are being investigated for applications such as permanent magnets, novel actuators, flux-guides for transformers, inductors, wireless charging applications, electromagnetic screening devices, electrical machines, motors and generators, and magnetic shielding purposes [1-5]. In these materials, the magnetic particles are uniformly dispersed in a polymeric matrix in order to reduce the cost and weight of components without sacrificing their magnetic behavior. Additionally, polymer composites can be manufactured through additive processes such as Fused Filament Fabrication (FFF), which allows to obtain components faster and with highly complex designs compared to magnetic composites manufactured with conventional processes. One of the main factors to consider in a permanent magnetic material application is the time dependence of the magnetic dipole moment volume density, which in the presence of a given field can be markedly affected because the magnetization decreases with time and its coercivity (H_c) is affected as well [1]. Consequently, their operation conditions change. Time dependent properties originate from thermally assisted processes of crossing an energy barrier that occurs when the applied field is suddenly reversed, and a significant amount of the particles is brought in a metastable state. By varying the field and field angle and monitoring the time dependence of the magnetic moment it is possible to determine the activation switching volume and energy barrier. Therefore, if this energy barrier is small, the time dependence is large and vice versa. For a composite with a normal distribution of switching fields the time dependent behavior is described by a logarithmic function as [6,7,8]:

[1]Corresponding author: tna30@txstate.edu

$$M(t) = M_o + S \cdot ln\left(1 + \frac{t}{t_o}\right) \quad (1)$$

Where M_o is the magnetic moment of the material just after the direction of the field is changed. S is the magnetic viscosity describing the time dependence of the magnetic moment. The parameter t_o is related to the time constant of the experiment and the materials properties but often considered a fitting constant [8]. It can be observed that the change in magnetic moment is large immediately after the field changes and then decreases over time. Time dependent measurements are typically done with a scalar instrument monitoring the sample's moment parallel to the applied field over time after a field change [9]. In this study, a biaxial Vibrating Sample Magnetometer (VSM) is employed to monitor both the M_x and M_y signal as a function of time. This is the first time that magnetic viscosities are studied with a vector VSM. In this study, we analyze the time dependence of Strontium Ferrite/PA12 filament composites for 3D printing purposes at 5wt% and 26wt% filling fractions.

EXPERIMENTAL PROCEDURE

Vestosint® 3D Z2773 from Evonik is used as the matrix of the filaments. It is a high quality PA12 with high mechanical properties and excellent chemical behavior certified for 3D printing. It was chosen because of its low water absorption and high melt flowability, which allows for high loading concentrations of magnetic particles compared to other polymers such as PLA. For the magnetic particles in the composite, OP-71 Strontium Ferrite ($SrO(Fe_2O_3)_6$) powder obtained from Dowa Electronics Materials Co. is used. Besides being a widely used material to create bonded magnets, strontium ferrite particles are very stable, non-toxic and reinforce the polymeric matrix. The average particle size of the powder is 1.4 µm and favors slight anisotropic behavior.

The composite filaments were made using a Thermo Fisher Process 11 Co-rotating Twin Screw Extruder, shown in Figure 1. It consists of two feeders, a water bath tray to cool down the extruded filament and an automatic spooling unit. The main process parameters include the temperature distribution in the barrel, the extrusion speed, the speed of the feeders with which magnetic powder and thermoplastic Nylon is fed into the barrel, and the measured back pressure.

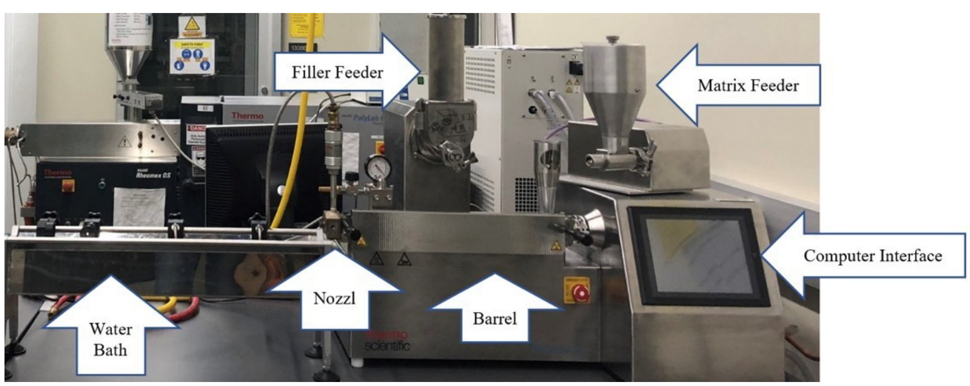

Fig. 1. Thermo Fisher Process 11 Twin Screw Extruder.

From the computer interface, parameters such as the temperature range, and the rpm of the screws and feeders are controlled. Eight temperature zones (Z) are manipulated during this experiment. Zone 1, Z_1, is permanently cooled and cannot be controlled. Z_2 to Z_6 go from 220°C to 240°C, at this stage of the process, the magnetic particles are added into the melted matrix. Z_7, Z_8 and the die go from 240°C to 230°C for extrusion. A vacuum pump connected to Z_7 of the extruder was used to prevent the formation of air voids in the magnetic filament, which is extruded through a 2mm nozzle and cooled down in a water bath. Consequently, the filament is spooled to obtain a uniform diameter of 1.2+/-0.5 mm with filling fraction of 5wt% and 26 wt% $SrO(Fe_2O_3)_6$. No evidence was found for an inhomogeneous distribution of the Strontium hexa-ferrite particles through the PA-12 matrix.

A MicroSense LLC/EZ9-HF VSM with a biaxial modified Mallinson coil set was used to determine the hysteresis curve and the time dependence of the magnetic moment of the filament samples at room temperature for different field angles. Additional measurements were performed on OP-71 strontium ferrite powder loaded in a Quantum Design powder sample holder. The biaxial coil set allowed for the measurements of the sample's magnetic moment parallel to the applied field (along the X-axis, M_x signal) and perpendicular to the applied field (along the Y axis, M_y signal). The magnetic hysteresis curves for both the M_x and M_y signals were measured in a field range from -22000 to 22000 Oe. Image effect correction is applied to all the measured hysteresis curves to compensate for the loss of magnetic signal as a function of the field when the saturation happens at values higher than 1.5T. Additionally, the sweep field lag was removed. This effect is the product of the lag in the data measured by the lockin amplifier. The magnetic moment of the sample rod is believed to be at least a factor 100 times smaller than the sample's magnetic moment and was not corrected for in the presented data. This vector approach allows for the determination of the magnetic anisotropy axis from the hysteresis data.

Time dependent measurements were done as a function of the reverse field and field angle. After saturation of the sample at 22000 Oe, the field was lowered to $-H_a$ and M_x and M_y were monitored for 300 seconds. The auto range functions of the lockin amplifier were used to guarantee an optimum sensitivity range and reduce the influence of digital noise. When analyzing the data, the values obtained during the first 10 seconds were ignored to remove the effect of the field transient on the measurement results [2]. The time constants of the lock-in amplifiers were set to 0.1 seconds and data was accumulated over 2 seconds for each data point.

RESULTS AND DISCUSSION

To check the homogeneity of our samples, the saturation magnetic moment density per unit mass was measured for different parts of the filament. VSM measurements were done on samples cut at different positions along the filament. Sample were slit along the cylindrical axis analyzing both sides of the fiber. The mass of each sample was measured with a scale down to a precision of 0.1 mg and used to determine the magnetic moment per unit mass. The standard deviation of the calculated magnetic moment per unit mass of five samples is similar in two digits to what one expects based on the digital error of the scale. This indicates that inhomogeneities in our composite are less than +/- 3%.

Fig. 2. (a) and (b) show the Hysteresis curve of the M_x and M_y signal of the 5wt% composite filament. The sample was positioned horizontally on the sample rod and the 0° orientation corresponds to the applied field being parallel to the cylindrical axis of the sample. The hysteresis curve of the M_x signal shows that at 90° the filament has the highest remanence, indicating the easy axis is oriented along this direction. Additionally, at 0° the material shows the lowest remanence, which means that the hard axis is found at this orientation. This suggest that the filament has a texture with the easy axis oriented along its radial direction. The graph shown in Fig. 2(b) of the M_y signal shows that the M_y hysteresis is also angle dependent and it confirms the anisotropy axis of the sample, with a negligible signal when the field angle is parallel to the easy or hard directions. The sign change of the M_y signal at 90° is due to a slight misalignment of the sample's easy axis with the field. The observed macroscopic anisotropy is uniaxial with the filament's cylindrical axis perpendicular to the easy-plane and parallel to the hard axis.

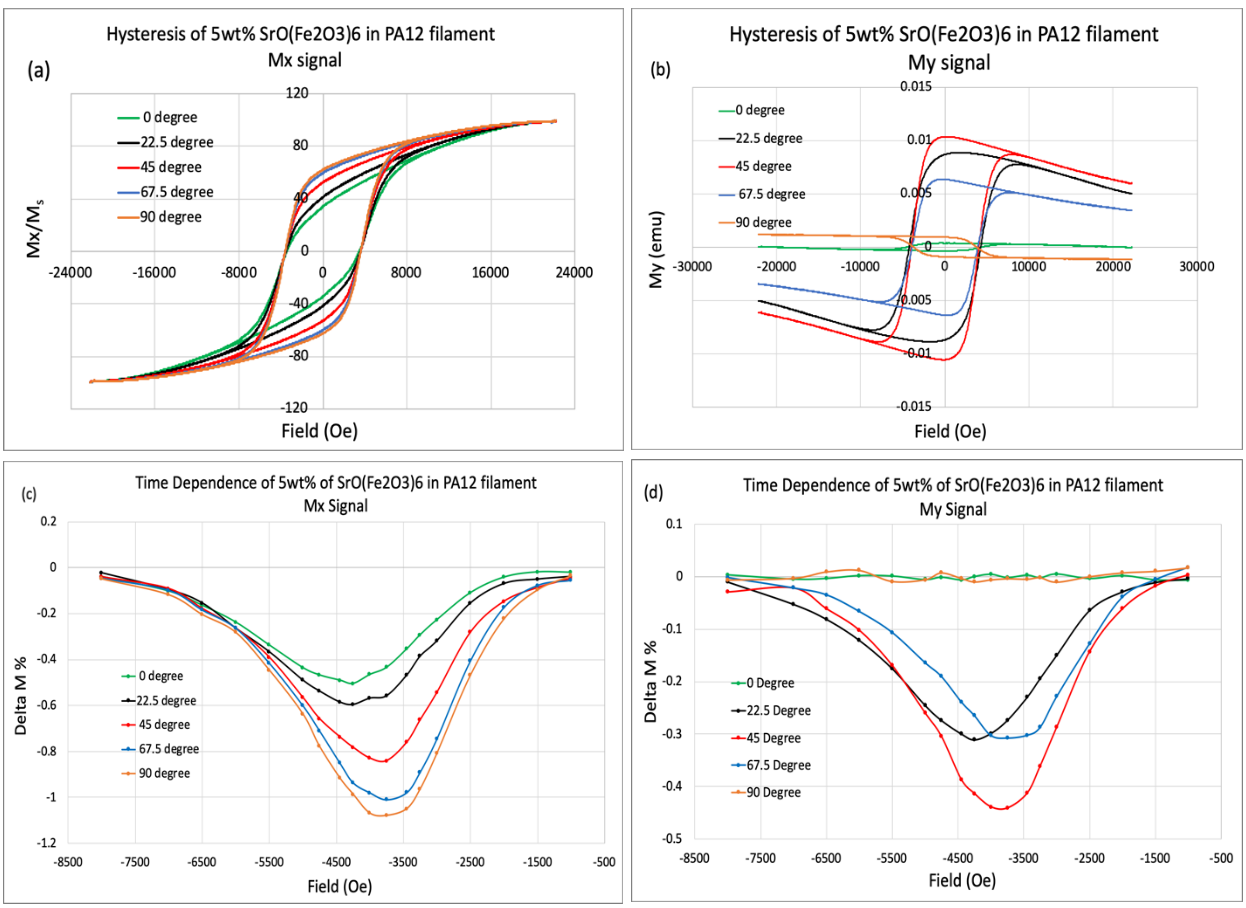

Fig. 2. M_x/M_s (a) and M_y (b) Hysteresis curves of the 5wt% $SrO(Fe_2O_3)_6$/PA12 filaments;
Time dependence of M_x/M_s (c) and M_y/M_s (d) signals of 5wt% $SrO(Fe_2O_3)_6$/PA12 filaments.

Fig. 2. (c) and (d) show the $\Delta M_x/M_s$ and $\Delta M_y/M_s$ measured over the first 300 seconds of the 5wt% composite filaments at 0, 22.5, 45, 67.5 and 90 degrees. The time dependence is largest for M_x when the sample is oriented along the easy axis, i.e. the field is perpendicular to the cylindrical axis of the filament. The time dependence of the M_y signal is the largest when the sample is

aligned at approximately 45° with respect to the easy axis and becomes zero when the field is parallel or perpendicular to the easy axis.

Fig. 3. summarizes the field angle dependence of the time dependent measurement on the 5wt% filament sample at RT. The M_x magnetic viscosity is maximum for field angles close to the easy axis and decreases for angles close to the hard axis to approximately half the value. The M_y magnetic viscosity is zero near the easy axis and hard axis and maximum for field angles of 45°.

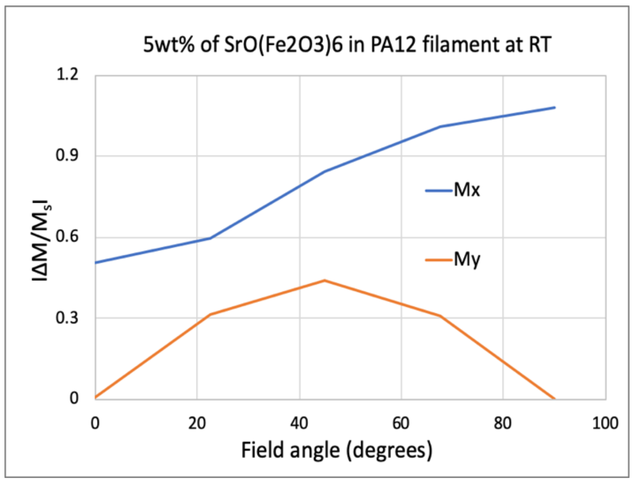

Fig. 3. | M/M_s| for 5wt% $SrO(Fe_2O_3)_6$/PA12 composite filaments at room temperature (RT).

Fig. 4. shows the M_x/M_s (a) and M_y (b) hysteresis curves and the M_x/M_s (c) and M_y/M_s (d) over the first 300 seconds after the field step of the 26wt% composite filament at different field angles. It can be observed that at 90°, the material has the highest remanence, and at 0° has the lowest remanence which reveals that the anisotropy of the higher packing fraction composite filament is similar to that of the 5wt% filament. The sign change of the M_y signal at 87 degrees in Fig. 4(b), is due to a slight misalignment of the sample's easy axis with the field. It is also clear that with the increase of filler content from 5wt% to 26wt%, the time dependence does not differ significantly which indicates negligible magnetostatic interactions between the particles. Additionally, the time dependence of the M_y signal changes sign as a function of the angle.

Similar experiments were performed on $SrO(Fe_2O_3)_6$ powder loaded in a 2 mm diameter cylindrical powder sample holder under a magnetic field of 22000 Oe. This sample differs in several ways from the magnetic composites: (1) the magnetic field induced anisotropy was much stronger and had more than one easy axis; (2) the packing fraction calculated from the sample's magnetic moment was close to 50% so the interaction of the magnetic particles with each other can no longer be ignored. The magnetic time dependent measurements differ in two important ways with the composite sample: (1) The magnetic viscosity in the x-direction is less field angle dependent and (2) the magnetic viscosity in the y-direction is changing sign with the field angle.

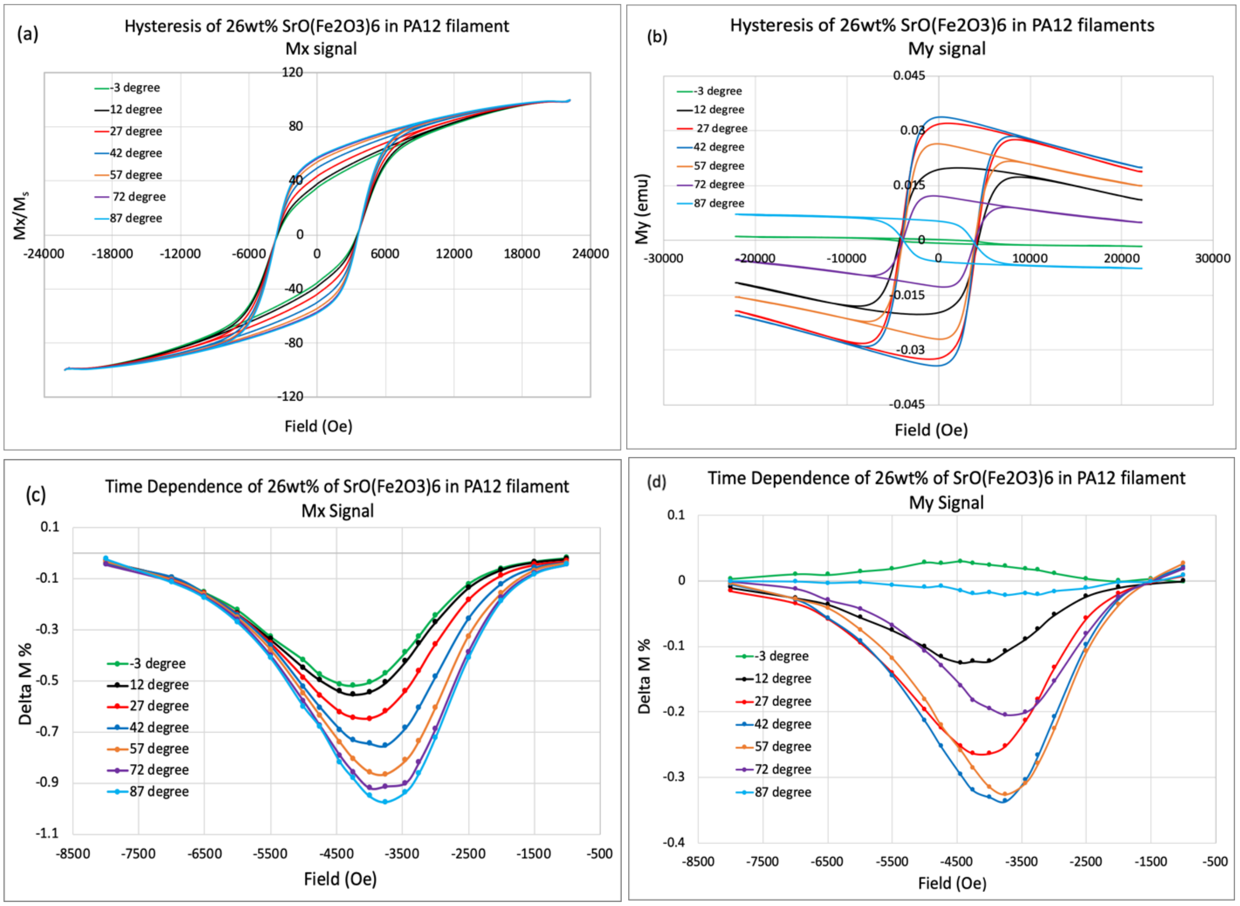

Fig. 4. M_x/M_s (a) and M_y (b) Hysteresis curves of the 26wt% $SrO(Fe_2O_3)_6$/PA12 filaments;
Time dependence of M_x/M_s (c) and M_y/M_s (d) signals of 26wt% $SrO(Fe_2O_3)_6$/PA12 filaments.

CONCLUSIONS

The hysteresis curve of the 5wt% and 26wt% $SrO(Fe_2O_3)_6$-PA12 filaments have their easy axis parallel to the radial direction, which means the filaments have a wire texture. This wire texture originates from the flow of the molten composites during the extrusion process. The Strontium hexa-ferrite has a hexagonal crystal structure affecting the shape of the powder's particles. Therefore, it is expected that the magnetic anisotropy and susceptibility of 3D printed samples is affected by the printing direction. This suggest that one must be able to optimize the materials properties by carefully choosing the infill direction when printing for example transformers [4].

We also presented the first vector time dependent measurements. The filament's time dependence is strongly sensitive to the field angle. The M_x viscosity collapses with a factor of 2 when the field is rotated from the easy plane to the hard axis. The extreme in the viscosity versus field curves shifts to larger field values for field angles closer to the hard axis. The interpretation of traditional scalar viscosity measurements is challenging and requires knowledge about the reversal mechanism (coherent versus incoherent reversal modes) to correctly interpret the magnetic activation volume. This might not be necessary when interpreting magnetic viscosity measurements performed with a biaxial VSM as at field angles close to the hard axis of the material, the coherent rotation is the expected reversal mechanism in the hexa-ferrite particles. We hope that the experimental data reported on in this paper will encourage modelling by theoreticians of vector viscosity measurements.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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