MAGNETIC CHARACTERIZATION OF 3D PRINTED HIGH-PERFORMANCE POLYAMIDE MAGNETIC COMPOSITE

Oluwasola K. Arigbabowo[*,1,2], Yash Tate[4], and Wilhelmus J Geerts[1,3]

Texas State University
601 University Drive, San Marcos, TX,78666
[1]Materials Science Engineering and Commercialization Program
[2]Ingram School of Engineering
[3]Department of Physics
[4]James Bowie High School, Austin
*Email: oka7@txstate.edu

Polyamide 4.6 is classified as a high-temperature thermoplastic because of its service temperatures of up to 175°C**,** bringing it close to high-temperature plastics like PPS or PEEK. Due to its high-temperature capability and price/performance ratio, Polyamide 4.6 is considered viable in developing high-performance bonded magnets by serving as a binder/matrix to magnetic powders/fillers to form multifunctional magneto polymeric composites that offer superior properties to conventional materials. In this research, 10 wt.% and 30 wt.% strontium ferrite magnetic powders were compounded with polyamide 4.6 using a co-rotating twin screw extruder to fabricate monofilament bonded magnets for 3D printing. Morphological and magnetic characterization was performed on the 3D printing monofilament samples using Scanning Electron Microscopy, and Vibrating Sample Magnetometer, respectively. The morphological observations showed an even dispersion of the strontium ferrite fillers in the magnetic composite. The magnetic hysteresis results obtained via the VSM measurement at elevated temperatures indicate that the polyamide 4.6 binder was durable enough to keep the magnetic particles from moving in the bonded magnets. This suggests that the strontium ferrite bonded with Polyamide 4.6 binder is a much better composite and can be used in high-temperature applications up to 150 °C.

Keywords: Magnetic fillers, Polyamide 4.6, Twin Screw Extrusion.

1. Introduction

Magnetic composites are a new trend of materials that consists of inorganic magnetic powders or particulates that serve as fillers or reinforcement embedded in an organic nonmagnetic matrix that serves as protection and host for the reinforcement [1, 2]. Among the magnetic fillers, iron oxides, which are classified as soft magnetic materials, have attracted significant interest. The common types of iron oxides are magnetite (Fe_3O_4) and maghemite (-Fe_2O_3), which have found numerous potential applications in magnetic recording technology, pigments, catalysis, photocatalysis, medical uses, and environmental processes. Generally, magnetic materials are broadly classified into permanent magnets (hard magnets) and soft magnets. Permanent magnets are characterized by high coercivity and low permeability, and due to this, they are quite challenging to demagnetize, and they store high energy [3]. The most common types of permanent magnetic materials are the rare-earth magnetic alloys, typically Samarium-Cobalt (SmCo) and

Neodymium-Iron-Boron (NdFeB) which are the best-performing ones, as they allow for a reduction of the component's dimension and weight due to their exceptional magnetic properties and high energy density. Other types of permanent magnetic materials are the hexagonal ferrites and common types of these ferrites are strontium ferrites and barium ferrites [4]. The primary advantage of the ferrites permanent magnetic materials is that unlike the rare earth types, they are available abundantly, which makes them more affordable. **Figure 1** shows a comparison chart of properties – operating temperature, magnetic strength, corrosion resistance and affordability, for the most common types of permanent magnetic materials, which can be used as selection matrix for specific applications.

Despite the high magnetic performance of permanent magnetic materials, they are quite expensive, chemically reactive, and typically fabricated via a sintering process, which makes them very brittle and exhibit poor mechanical properties. The sintering process of permanent magnetic materials mounts a gross limitation and difficulty to shape in complicated geometries, thereby posing a huge restriction in manufacturing flexibility and suitability for near-shape processing. In order to solve the fundamental challenges and shortcomings of sintered magnetic materials such as brittleness, corrosion, and manufacturing flexibility of complex magnetic devices, a viable approach known as “bonded magnets” is being widely considered.

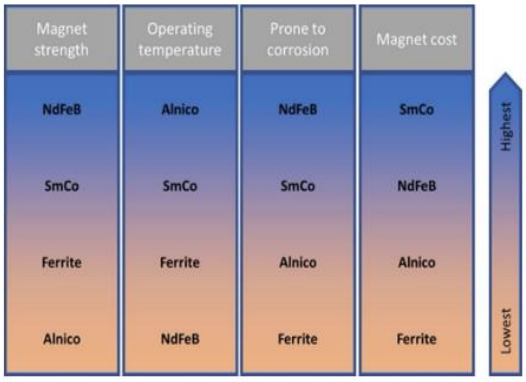


Figure 1. Selection matrix for permanent magnetic materials [5].

Bonded magnets are magnetic composites fabricated by bonding a high packing fraction of permanent magnetic fillers with a polymer binder by using different polymer processing technologies. Based on the type of polymer binder – elastomer, thermosets, or thermoplastics, the different polymer processing technologies that are typically used in the fabrication of bonded magnets are compression molding, injection molding or extrusion process. The extrusion process is a viable process for thermoplastics [6] and has exhibited a high potential for fabricating an anisotropic and high-performance bonded magnet.

High-performance bonded magnets are fabricated using high performance binders such as high temperature thermoplastics like polyetheretherketone (PEEK), Polyphenylene sulphone (PPS), polyetherimide (PEI), and high-performance polyamides (HPPA). The high-performance binders are classified as high-temperature thermoplastics because of their heat resistance over the long term at service temperatures greater than 150°C and short-term use at temperatures greater than 250° [7]. The thermal integrity exhibited by high temperature binders would facilitate the restriction of magnetic fillers in bonded magnets when exposed to elevated temperature, thereby

facilitating the fabrication of high-performance bonded magnets that can withstand high temperatures such as in electric motors and sensors in electric cars and automotive applications. As illustrated in **Figure 2**, other common applications for high performance bonded magnets are magnetic robots for drug delivery biomedical applications and 3D printed Halbach cylinder for portable MRI scanner used in diagnostic imaging.

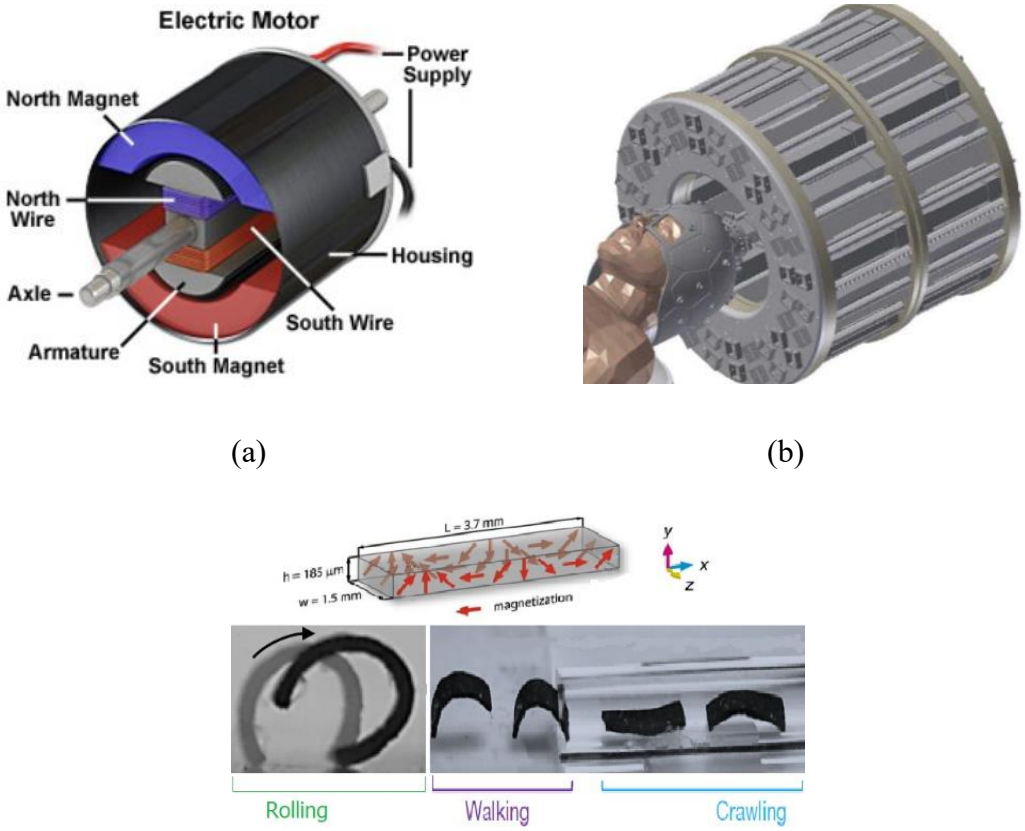


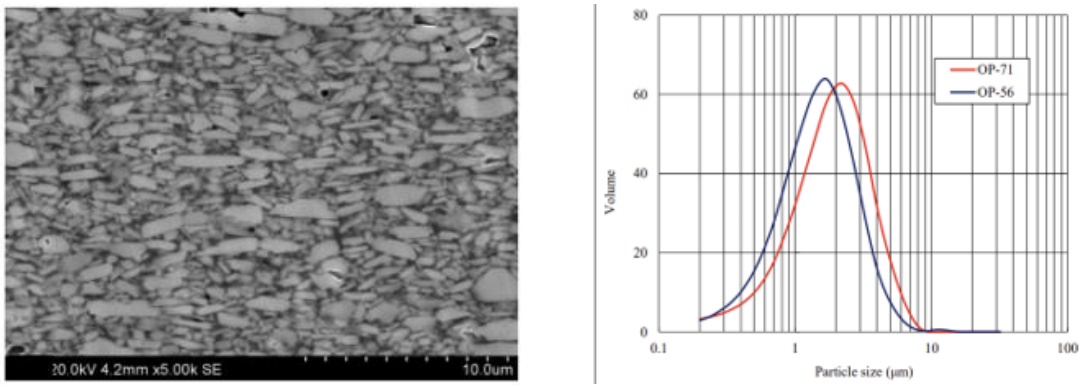
Figure 2. Common applications of bonded magnets (a) Electric motors [8] (b) 3D printed Halbach cylinder for Portable MRI scanner [9] (c) magnetic robots for drug delivery [10]

In this research, we have demonstrated the fabrication of high performance bonded magnetic composites monofilaments using the twin screw extrusion polymer processing technology, which is viable for 3D printing fused filament fabrication process. In addition, materials characterization such as morphological and magnetic measurement were carried out on the 3D printing monofilaments bonded magnets to evaluate its magnetic performance.

2. Materials and Methods

2.1 Materials

The magnetic filler used in this research is a strontium ferrite magnetic powder as obtained from DOWA electronics. As shown in the morphological observation in **Figure 3**, the ferrite powders exhibit a platelets shape, and the average particle size was reported as 0.99 um.



(a) (b)

Figure 3. (a) SEM morphology of strontium ferrite powders (b) Particle size distribution [11]

The binder used in developing the bonded magnets is a high temperature thermoplastic known as Polyamide (PA) 4.6, also known as Nylon 4.6, which was supplied in pellets form by premier plastics. Polyamide 4.6 belongs to the class of high-performance polyamides, which can sustain high stresses at elevated temperatures. It is also chemically non-reactive and can withstand exposure to aggressive environment, which makes it suitable for under-the-hood automotive applications. Polyamide 4.6 is chemically classified as an aliphatic type of polyamide, which resulted from polycondensation reactions of 2 monomers – 1,4- diaminobutate, with 4 carbon atoms, and adipic acid with 6 carbon atoms, thereby resulting in Nylon 4.6. The heat resistance properties and thermal integrity of Polyamide 4.6 can be attributed to the higher number of amide groups per given monomeric chain length and higher symmetry in its chain structure. This also increases its crystallinity and dimensional stability. The table below shows the materials properties of Polyamide 4.6 according to the technical data sheet of the product as received from the supplier.

Properties	Values
Density (g/cm^3)	1.18
Tensile Strength (MPa)	103
Tensile Modulus (GPa)	3.2
Flexural Modulus (GPa)	3.1
Glass transition temperature (°C)	85
Melting temperature (°C)	295
Heat deflection temperature (°C)	160

2.2 Fabrication of bonded magnets

Approximately, 10 and 30 wt.% packing fractions of the strontium ferrite magnetic fillers were compounded with the polyamide 4.6 thermoplastic binder using a process 11 twin screw extruder shown in **Figure 4**. The magnetic fillers were side fed in the twin screw extruder to enable its proper dispersion in an already melted polyamide 4.6 matrix prior to the side feeding. The shear intensiveness of the twin screw extrusion process facilitated a homogenous and well compounded bonded magnet, which was fabricated in a monofilament form with an average diameter of 1.75 ± 0.05 mm viable for a fused filament fabrication 3D printing process.

Figure 4. Process 11 twin screw extruder

3. Materials Characterization

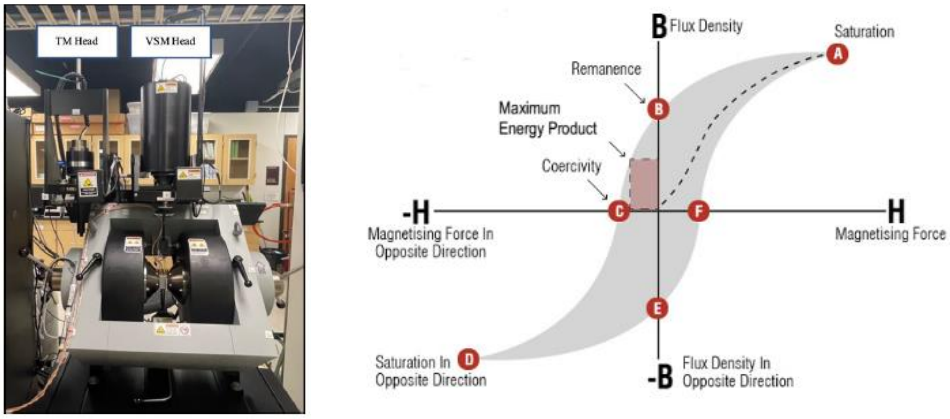
3.1 Scanning electron microscopy

The microstructural studies of the bonded magnets were interrogated using a scanning electron microscope to evaluate the morphology and dispersion state of the strontium ferrite magnetic powders in the polyamide 4.6 matrix. The SEM samples investigated were intrinsically nonconductive, which enabled accumulation of electrons on them, thereby leading to blurry SEM imaging. This was addressed by coating the SEM samples with a 2 nm gold conductive layer using a sputter coater, to enable better SEM imaging. The SEM investigation was carried out on cross sections of the monofilament bonded magnets to evaluate the composition and morphology of the magnetic composite.

3.2 Magnetic characterization

The magnetic characteristics of the bonded magnets 3D printing monofilaments were characterized using a biaxial vibrating sample magnetometer (VSM) shown in **Figure 5a**. The magnetic hysteresis was obtained from the VSM measurement between room temperature 25 C to 150 C, to interrogate the effect of temperature on the magnetic properties of the strontium ferrite bonded magnets. The hysteresis loop was obtained via a sweep mode using an applied magnetic field strength from -22kOe to 22kOe and a sweep rate of 400 Oe/s. **Figure 5b** shows a typical magnetic hysteresis loop, which describes the common magnetic properties associated with magnetic materials. The maximum induced magnetization (shown as A on the loop) by the applied magnetic field is known as saturation magnetization *(M_s)*. This induced magnetization remaining (shown as B on the loop) after the removal of the applied field is referred to remanent

magnetization *(M_r)*. The magnetic field required to demagnetize the magnetic material (shown as C on the loop) or revert magnetization to zero is known as magnetic coercivity *(H_c)* [12].



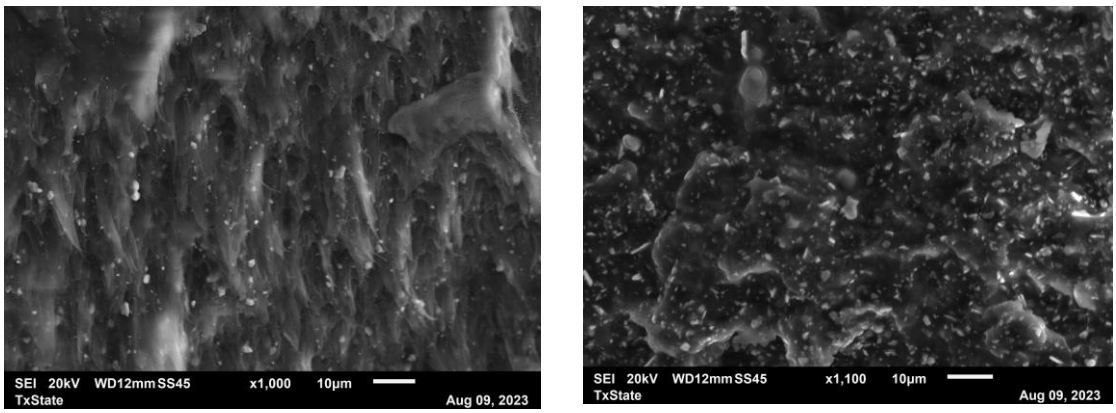
(a) (b)

Figure 5. (a) Biaxial vibrating sample magnetometer (b) Magnetic hysteresis loop [13]

4. Results and Discussion

4.1 Morphological studies

The SEM images presented in **Figure 6** illustrate the morphology of the 10 wt.% and 30 wt.% packing fraction of strontium ferrites in the bonded magnetic composites. The platelet shaped structures of the ferrite powders were observed to be evenly dispersed throughout the polyamide 4.6 matrix binder. A uniform dispersion is very essential for the interfacial bonding between the magnetic filler and the binder, which enhances the homogeneity and facilitates an even distribution of the magnetic domain sites in the magnetic composites.

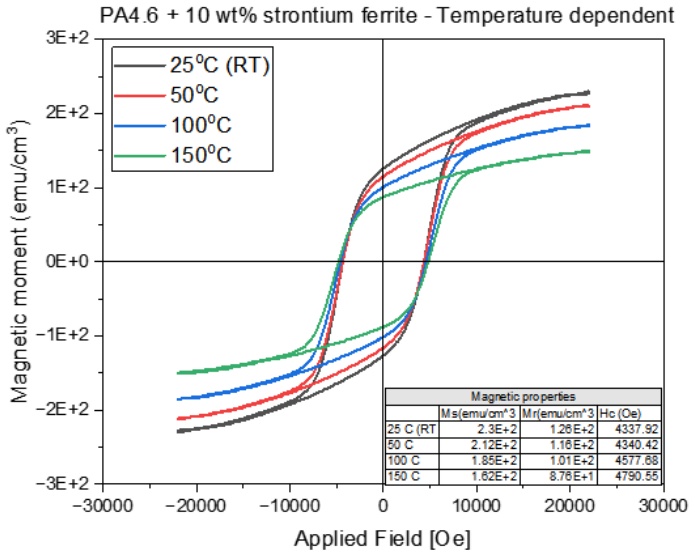


(a) (b)

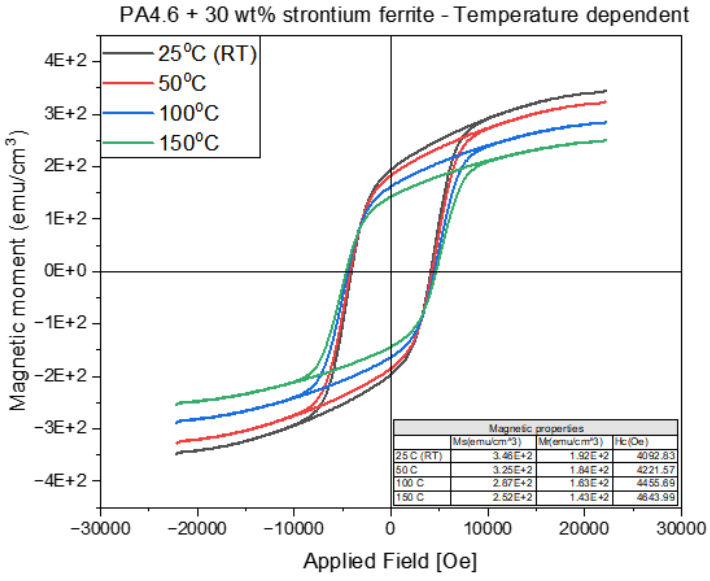
Figure 6. Scanning electron microscopy images of (a) 10 wt.% strontium ferrites magnetic composite (b) 30 wt.% strontium ferrites magnetic composite

4.2 Magnetic performance

The magnetic hysteresis loops obtained from the VSM measurements are presented in **Figure 7a** and **Figure 7b** for 10 wt.% and 30 wt.% strontium ferrite bonded magnets respectively. The magnetic hysteresis loops shown in **Figure 7** are plots of magnetic moment normalized to the volume of the strontium ferrite as a function of the applied magnetic field. The magnetic properties evaluated are the saturation magnetization, remanent magnetization, and the coercive field, which were investigated at different temperatures, ranging from room temperature (25 °C) to 150 °C.



(a)



(b)

Figure 7. Magnetic hysteresis loop VSM measurement of PA 4.6 bonded magnetic composite at elevated temperature

The saturation magnetization indicates the maximum induced magnetization achieved by the bonded magnets during the magnetization sweeps measurement. It can be observed from **Figure 7** that the saturation magnetization Ms, reduces with increasing temperature, with a maximum reduction observed at 150 ºC. A similar trend was also observed with the remanent magnetization Mr, however at a lower reduction rate compared to Ms. The remanent magnetization is an important property of magnetic materials, as it indicates the remaining induced magnetization when the applied field reverts to 0. The reduction in the Ms and Mr observed from the strontium ferrite bonded magnets in **Figure 7** could be attributed to decrease in the magnetic dipole moment of the strontium ferrite at elevated temperatures, which becomes more difficult to rotate. The magnetic coercivity or coercive field of the bonded magnets were observed to increase with increasing temperature. The observed trend in coercivity of the bonded magnets indicates the high resistance to external magnetic field as the field required to demagnetize the bonded magnets increases with temperature. This increment in the coercivity exhibited by the strontium ferrite bonded magnets is a typical behavior of permanent magnetic materials.

5. Conclusion

Strontium ferrite bonded magnetic composites was fabricated via twin screw extrusion technology using a polyamide 4.6 binder to produce a high-performance bonded magnet. The bonded magnets were fabricated into a monofilament with a diameter of 1.75 ± 0.05 mm which is viable for 3D printing fused filament fabrication.

The morphological studies showed an even dispersion of the strontium ferrite magnetic fillers in the polyamide 4.6 matrix binder, which would facilitate an efficient interfacial bonding in the bonded magnets composite.

Magnetic hysteresis loops from room temperature to 150 ºC were obtained using a biaxial vibrating sample magnetometer (VSM) to evaluate the effects of elevated temperature on the magnetic characteristics of the fabricated bonded magnets. It was observed that the saturation and remanence magnetization reduce with increasing temperature. This reduction can be ascribed to a decrease in magnetic dipole moment of the strontium ferrite with increasing temperature. Interestingly, coercivity was observed to increase with increasing temperature, which indicates that the fabricated bonded magnets will become a more permanent magnet at higher temperature. This implies that that the polyamide 4.6 binder was durable enough to lock the orientations of the magnetic particles from moving in the bonded magnets which suggests that strontium ferrite bonded with Polyamide 4.6 binder is a much better magnetic composite and can be used in high-temperature applications up to 150 °C when compared to strontium ferrite and polyamide 12 bonded magnetic composites.

The fabricated strontium ferrite bonded magnets monofilaments in this research have exhibited potential as a viable magnetic material that can be used in additive manufacturing of 2D and 3D magnetic structures. 3D printing of the fabricated bonded magnets would enable alignment of the magnetic particles, thereby further enhancing its magnetic performance. Also, the mechanical properties characterization to evaluate the structural integrity of the bonded magnets is worth investigating.

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7. References

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