Solid Freeform Fabrication 2024: Proceedings of the 35th Annual International
Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference

High-temperature 3D printing of Polyamide Magnetic Composites

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Bonded magnetic composites (BMC) offer greater feasibility than sintered magnets due to their low density, resistance to corrosion, and suitability for additive manufacturing processes. On a 3D printer, manufacturing BMC using polymers like polyether ether ketone (PEEK) and polyamide requires printing at higher temperatures, presenting challenges such as uneven bed adhesion and possibly damaging printer components. Our study focuses on modifying an off-the-shelf desktop 3D printer by incorporating a high-temperature nozzle and an enhanced bed heating unit for high-temperature fused filament fabrication applications. Composite filaments are produced using the twin screw extrusion technique, employing polyamide 4.6 as the binder matrix and Strontium ferrite powder as a filler. This combination yields robust magnetic properties. Magnetic properties assessed using a vibrating sample magnetometer demonstrate a difference in remanence (Mr), indicating the potential utility of BMC as permanent magnets.

Keywords: Bonded magnetic composites, high-performance polymer, Fused Filament Fabrication, magnetic composites, High-temperature 3D printing.

1.0 Introduction

Polymer magnetic composites are materials that are traditional polymers with magnetic fillers, producing a robust combination with superior magnetic and mechanical properties. These polymer magnetic composites can be made not only by conventional manufacturing techniques such as calendaring, injection molding, and extrusion molding but also by additive manufacturing. 3D printing, also known as layered manufacturing, is an emerging fabrication technology that builds products layer by layer using a numerically controlled system. This process allows for various materials with complex shapes and a smoother surface. Additive Manufacturing (AM) is renowned for its ease of use, high flexibility, and user-friendly interface. This process produces a wide range of materials with a fine surface finish and intricate shapes. AM processes are divided into seven approaches. These seven methods are (i) Binder jetting technology, which selectively deposits a liquid bonding chemical to combine powder constituents. (ii) The directed energy deposition (DED) approach in AM uses fusing of the print material by melting on site (iii) Material extrusion is a procedure in additive manufacturing that systematically dispenses material through a nozzle. (iv) Material jetting is an AM process that selectively deposits and builds material droplets. It is used with materials like wax, which have a low melting point. (v) Powder bed fusion is an AM technique employing heat energy to fuse powder bed sections selectively. It is most widely used today and is popular because of its rapid product manufacturing time. (vi) Sheet lamination is an AM process that bonds material layers to create an object. (vii) Vat photopolymerization is an AM technique that uses photo-initiated liquid photopolymer in a vat using polymerization activated by digitized UV light [3].

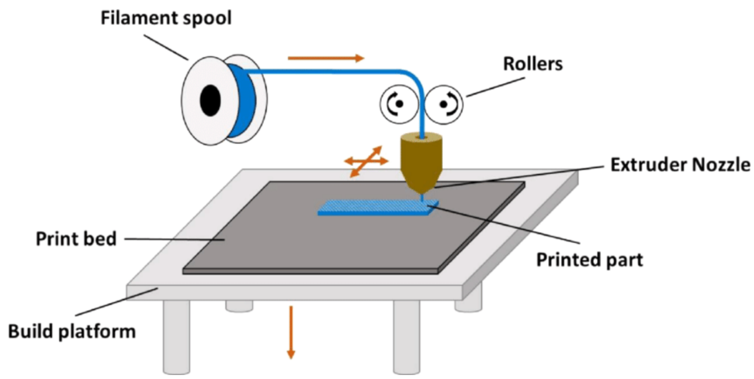


Figure 1: Diagram of FFF process [1]

Each additive manufacturing approach has advantages, but the most prominent and globally used technology is Fused Filament Fabrication, also known as Fused Deposition modeling (FDM). FFF is the most feasible and price-effective method for producing parts. It is a reliable and user-friendly method that can be installed in office environments. FFF is most compatible with thermoplastic polymer filaments, as shown in Figure 1. The process involves utilizing filaments as the primary material and employing a nozzle with a heating mechanism. This mechanism melts the filament and deposits it onto the print bed, allowing for the gradual formation of the part through a layer-by-layer deposition process, moving the extrusion nozzle with a computer-controlled X, Y, and Z-stage. The speed of the FFF printing process is contingent upon the height of each layer deposited. The term "vertical deposition rate" delineates the quantity of material added to the FFF machine in a single pass along the vertical axis. The layer height, also known as the thickness of each layer, is a crucial part that directly influences the quality of the printed part [2]. The Z axis affects the structure of the printed part as layers stack on each other. Currently, there is a limitation of readily accessible filaments and printers in the market that allow users to print bonded magnets using additive manufacturing. However, several investigations in the current research field involve using 3D-printed polymer composites that incorporate rigid magnetic particles such as NiZn, Strontium ferrite, and Neodymium Iron Boron (NdFeB) [4,5,10,11]. Although NdFeB has a more significant magnetic moment per unit volume, Strontium Ferrite possesses multiple benefits compared to Neodymium-based magnets among these magnetic particles. For example, SrFe12O19 exhibits exceptional thermal robustness, maintaining its magnetic characteristics at elevated temperatures in contrast with NdFeB, and is also much cheaper, so currently, most permanent magnets used in applications are made of SrFe12O19.

Bonded Magnetic composites use polymers as matrix, exhibiting different properties depending on mechanical and thermal properties. Using these benefits of polymeric materials, such as affordability, manufacturability, and lightweight advantages, suitable engineering thermoplastics or thermosets can serve as a matrix or binder for magnetic particles to fabricate a BMC. Polyamides, known as nylons, have been widely considered suitable engineering thermoplastics for developing BMCs. This high-performance polymer enables us to manufacture diverse products with a more refined surface finish and complex forms, as shown in Figure 2. Polyamides, often called Nylons, are categorized into many varieties, including Nylon 12, 6, 6, 6, and 4.6. AM is highly customizable and easy to use. The additive manufacturing process uses a wide variety of polymers. These polymer materials possess a partially crystalline structure and demonstrate a favorable amalgamation of material characteristics. Although the matrix used in producing bonded magnetic composite generally does not directly affect the overall magnetic properties, the packing density and the orientation distribution of the anisotropic particles in the composite can significantly affect the remanence and, thus, the energy product of bonded magnets. The materials used also affect the overall magnetic properties. Polymeric materials such as Acrylonitrile Butadiene Styrene (ABS) and Thermoplastic Polyurethane (TPU) have retained magnetic properties when processed through FFF due to their inherent mechanical properties and low processing temperatures. [8]

Matrix contains magnetic particles in bonded magnetic composites; rare earth materials like neodymium iron boron or SmCo, Alnico particles, or hard magnetic ferrites are infused in the matrix of bonded permanent magnets to make them magnetic. Attempts to use ceramic powders such as barium hexaferrite or strontium hexaferrite for their ferrite nature have resulted in magnetic composites with enhanced magnetic properties like coercivity and large stored energy, although having an impact on mechanical properties [18].

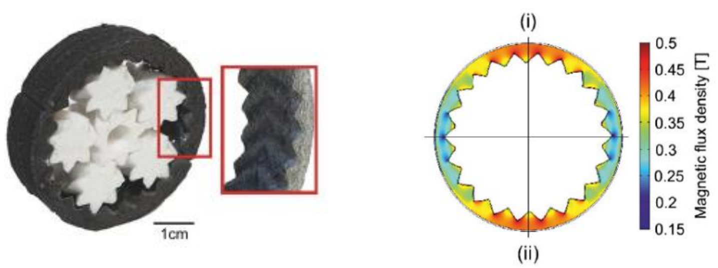


Figure 2: 3D printed bonded Magnetic gears with variable magnetic flux density [2]

Introducing anisotropic magnetic fillers to a polymer matrix results in the modification of its mechanical properties. This includes variations in ultimate tensile strength and young's modulus due to the magnetic filler's anisotropic nature [7]. These filters are also responsible for promising magnetic remanence, coercivity, and sometimes promising magnetic energy products. Additionally, it's worth noting that the FFF (Fused Filament Fabrication) method does not alter the inherent structure during the manufacturing of bonded magnetic composites [5]. While utilizing FFF and achieving desired results, it is crucial to adjust 3D printing parameters, including nozzle temperature, layer thickness, infill pattern, shell layer thickness, and orientation. The magnetic properties are significantly influenced by both infill and print patterns. It is directly proportional to the magnetic moment the produced composite exerts, which affects its magnetic properties. This can produce 3D-printed magnetic composites with enhanced magnetic performance [12]. Gandhala et al. [13] 3D printed bonded magnets using the big area additive manufacturing (BAAM) technique. Utilizing polyamide 12 polymer and Sm-Fe-N as a magnetic additive, a mechanical test performed on 3D-printed composites determined that adding magnetic filler led to variability in ultimate tensile strength and Young's modulus due to the anisotropy of magnetic fillers. Also, a morphological study using XRD showed no phase change of Sm-Fe-N additives, and the post-magnetic alignment of the printed sample showed an increase in remanence in parallel orientation.

High-temperature 3D-printed bonded magnets can significantly change several advanced industries, such as aerospace, automotive, and renewable energy systems. These magnets can improve the performance and efficiency of engines in electric vehicles, increase the reliability of wind turbines, boost the performance of motors and sensors in harsh situations, and make products with complex shapes and sizes [19].

This research is focused on creating high-performance bonded magnetic composites using a modified high-temperature 3D printer and optimizing the composite fused filament fabrication process. To understand pre- and post-printing composite properties, characterization tests, including morphological and magnetic measurements, were performed on the filament and 3D-printed bonded magnets.

2.0 Materials and Experimentation

The composite filament used in this study consisted of Polyamide 4.6, a polycondensation product of tetramethylene diamine and adipic acid, and Strontium ferrite powder (OP-56) as the filler material. The Strontium ferrite powder, a hexaferrite ceramic powder with a platelet structure, was obtained from Dow Electronics and incorporated at 10 and 30 wt.% packing fractions with the polyamide 4.6 thermoplastic matrix using a Themo Scientific Process 11 twin-screw extruder. Magnetic fillers were introduced from the side feeder after the matrix was melted to ensure proper dispersion. The shear and thermal forces generated during the twin-screw extrusion process result in homogeneous and well-dispersed composite filament with an average diameter of 1.74 mm, suitable for 3D printing processes.

An off-the-shelf LulzBot TAZ 5 3D printer was modified to print at elevated temperatures up to 370 °C using 1.75mm-2 mm filaments. The setup is shown in Fig. 3 below. The printer allows for printing functional prototypes, manufacturing aids, and print-on-demand parts.

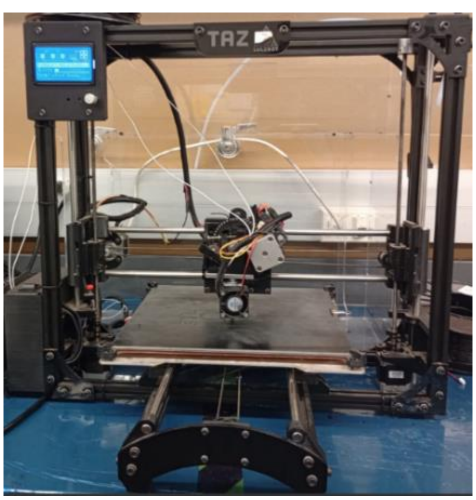
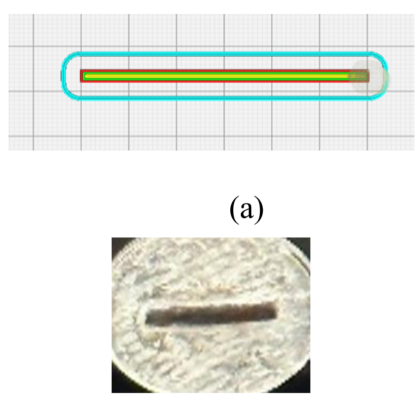


Figure 3: Modified high-temperature 3dprinter



(a)

(b)

Figure 4: (a) Cura LE sliced file (b) printed line sample

The original extrusion nozzle was replaced with a super volcano-hardened steel nozzle, increasing volumetric flow [9]. This replacement reduces the risk of nozzle clogging and improves the uniform heating and melting of the composite filament, resulting in a consistently uniform extruded layer from the nozzle. Due to the composite's high melting temperature, achieving proper adhesion to the print bed proved challenging. To address this issue, an E3D high-temperature silicone bed heater was installed, enabling the bed temperature to be increased to 135°C.

The line samples for both 10 and 30 wt. % were designed in Autodesk Fusion 360 with a 2 mm diameter and 5 mm length dimension and sliced using a Cura LE slicer to convert into a printable sliced file. **Figure 4(a)** shows an image of the sliced file, and Figure 4(b) shows an image of the printed line sample glued to an 8 mm cover glass slide Both loadings of Strontium ferrite were printed using the modified printer at 355 °C bed temperature 135° The layer height is 0.2 mm, and since the bonded composite's infill factor affects the saturation magnetization, i.e., in proportion to the infill density factor, a 100% infill was selected for the printing line sample. The Polyamide 4.6 polymer binder is hygroscopic, the filament was dried before printing to ensure no moisture is trapped in the matrix, which can affect the printing process. The printing process was carried out at 20 mm/s and a flow rate of 130% to minimize the void formation and clogging of the nozzle.

3. Materials Characterization

3.0 Morphological characterization

The morphological testing of the bonded magnetic composite filament and 3D printed samples was performed utilizing a JOEL scanning electron microscope, and the evaluation of the dispersion of the strontium ferrite magnetic powders in the polyamide 4.6 matrices was recorded. The SEM samples investigated are non-conductive due to their thermoplastic Polymer matrix, which resulted in the accumulation of electrons during SEM imaging. This was addressed by coating the SEM samples with a 2 nm gold conductive layer using a sputter coater to avoid charging effects that negatively impact imaging quality. The SEM investigation was carried out on cross-sections of the bonded magnetic filament and 3D-printed samples to evaluate the composition and morphology of the magnetic composite.

3.1 Magnetic performance

Magnetic characteristics were observed in the Vibrating Sample Magnetometer (VSM) Figure 5 for 10 and 30 wt. % filament and printed samples. The sample was mounted with its cylindrical axis horizontally on a quarts 8 mm rod as shown in the left image in Figure 5 below. Measurements were taken as a function of the field angle from zero to 360 degrees with increments of 15 degrees. The zero-degree measurement corresponds with a field direction parallel to the cylindrical axis of the (printed) filament. At each angle, the hysteresis curve was measured from -2.2 to +2.2 Tesla with a sweep rate of 400 Oe/s. The raw hysteresis curve data was corrected for the image effect and the field lag. The former correction was done to compensate for the loss of magnetic signal because of the disappearance of the magnetic images of the sample in the pole pieces during the saturation of the pole pieces above 15000 Oe.

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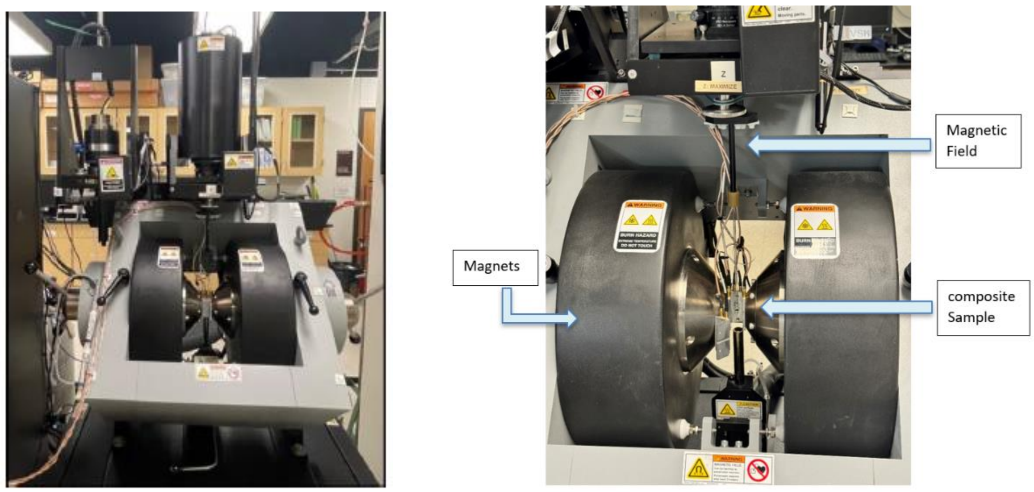
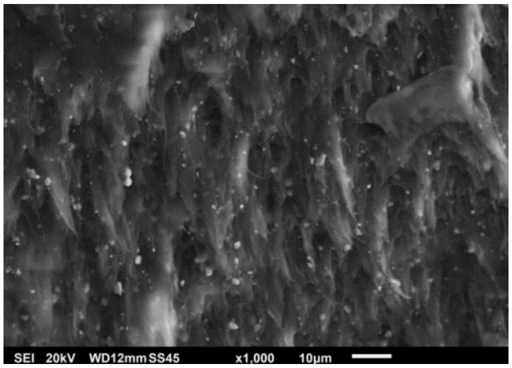


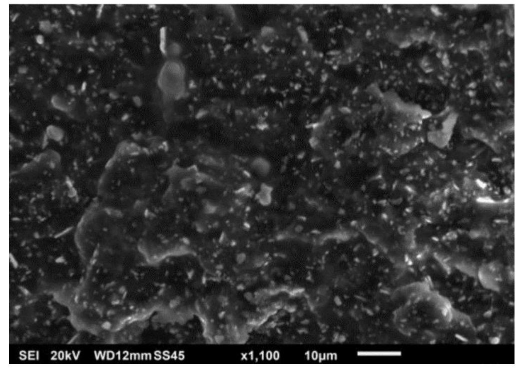
Figure 5: Vibrating Sample Magnetometer (VSM)

4.0 Result and Discussion

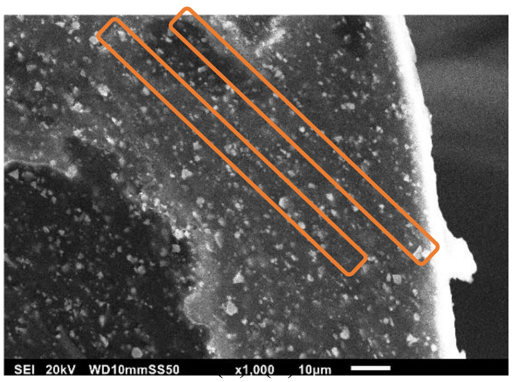
4.1 Morphological study

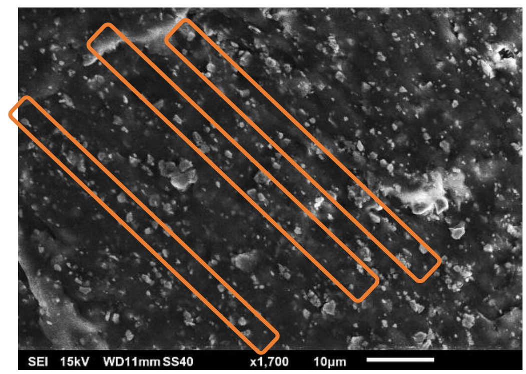
The filaments and print samples had a smooth finish with no internal deformations. The SEM images in Figure 6 illustrate the morphology of the 10 and 30 wt.% loading of strontium ferrites powder in the bonded magnetic composites. Filler powder can be observed in platelet structures. In filament, figure 6 (a) (b) [14]. Platelets are evenly dispersed within the polyamide 4.6 polymer matrix. To ensure optimal performance, it is imperative to achieve a uniform dispersion, thereby strengthening the interfacial bonding between the magnetic filler and the binder, as the accumulation of filler material will lead to the clustering of magnetic domains. This process promotes homogeneity and facilitates the even distribution of magnetic particle sites within the magnetic composites, avoiding instances of accumulation of magnetic particles with little polymer in between, which would weaken the mechanical properties. Figures 6 (c) and (d) show the alignment of strontium ferrite platelets in a printed composite; there is also a distinct alignment of strontium ferrite filler in printed composites. This alignment can be attributed to shear flow induced by the nozzle while printing a semi-liquid state composite, which changes with layer height and nozzle diameter [11]. The nozzle aligns filler material in a specific direction.





(a) (b)



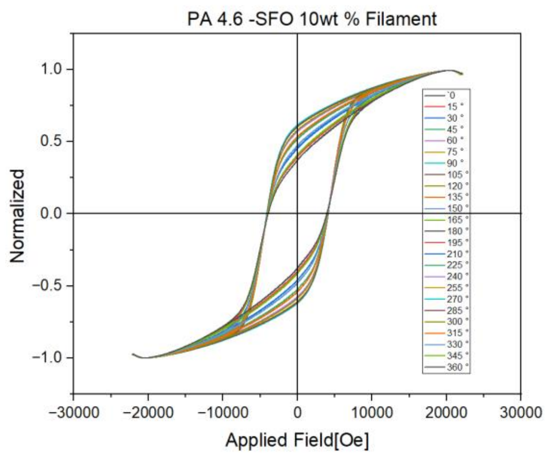


(c) (d)

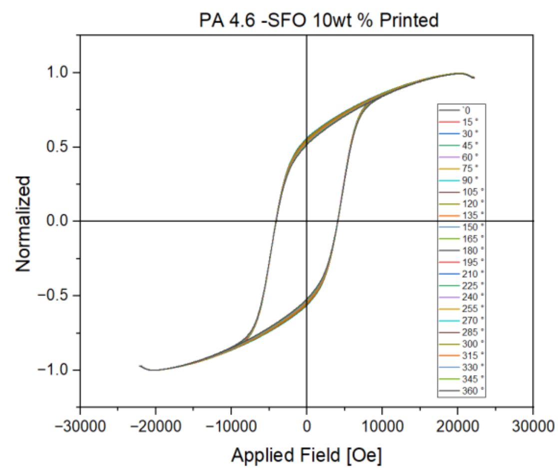
Figure 6:- (a) 10 wt. % PA 4.6- Strontium ferrite Filament. (b) 30wt% % PA 4.6- Strontium ferrite filament. (c) 30 wt. % PA 4.6- Strontium ferrite filament3D printed. (d) 30 wt. % PA 4.6- Strontium ferrite printed.

4.2 Magnetic characterization.

Magnetic measurements of filament and printed sample resulted in a hysteresis graph, which denotes magnetic values of Magnetic remanence (Mr.), intrinsic Coercivity field (Hc), and saturation Magnetization (Ms). These values are vital to determine the magnetic performance of the magnetic material. It can be observed when comparing **Figure [7](a)(b)** filament to **Figure [7] (c)(d)** printed samples the magnetic hysteresis loop of the PA 4.6 + SFO 10 and 30 wt. % filament shows a more significant field angle dependence compared to the 3D printed sample, which can be attributed to the different alignment of the acicular strontium ferrite particles in the composite during the extrusion process. This alignment is because of the shear flow on the orientation of the SF platelets, which align them near the cylindrical surface with their easy magnetic axis along the radial direction of the extruded filament. The alignment in the center is less strong [16]. The shear flow is different for the twin screw extruder's die and the 3D printer's hot nozzle. The flow of filler material in the composite is affected by the extrusion diameter and extrusion speed, which are different for the 3D and the twin-screw extruder; results highlight that alignment forces acting in the printer extruder are smaller than in the twin-screw extruder and affect the magnetic properties. Both filament and 3d printed composites exhibit magneto-crystalline anisotropy depending on the orientation of the sample in a magnetic field, resulting in distinct easy and hard; the hard axis is the direction in material that requires a higher amount of energy to get magnetized, which is conveyed by the applied field.



(a)



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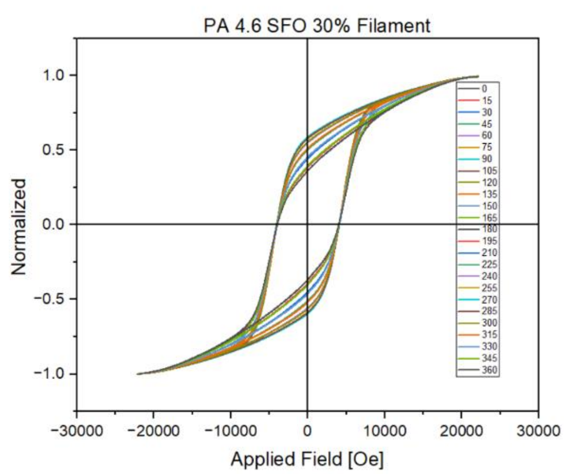
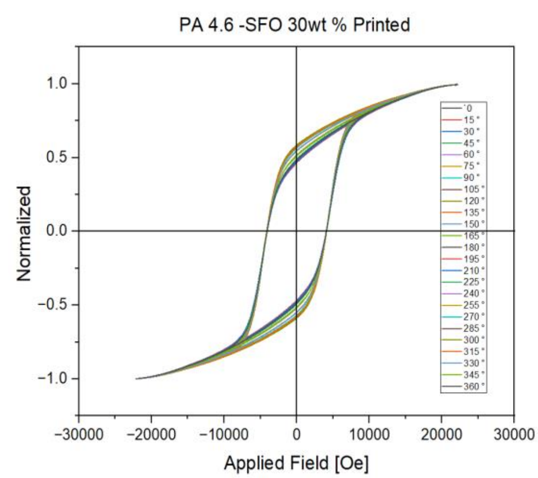


(c)

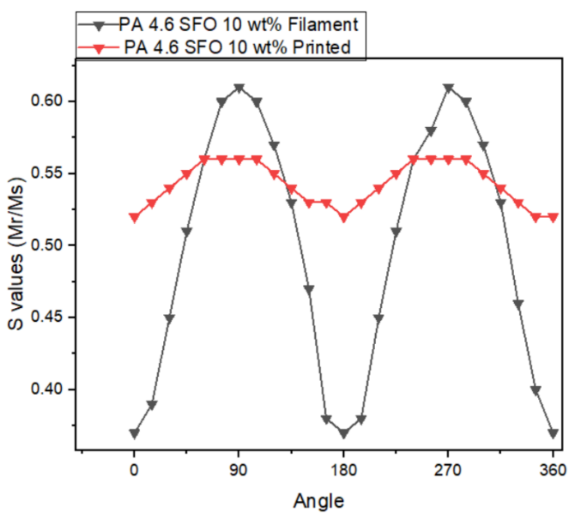


(d)

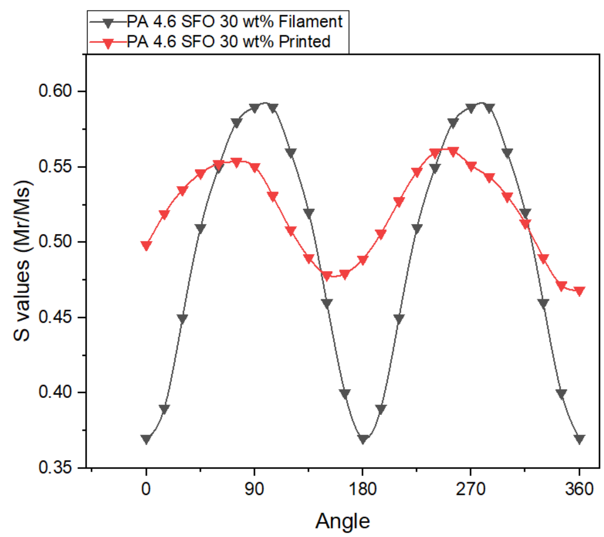
Figure 7:- (a) 10 wt. % PA 4.6- Strontium ferrite Filament. (b) 10wt% % PA 4.6- Strontium ferrite printed. (b) 30 wt. % PA 4.6- Strontium ferrite Filament. (d) 30 wt. % PA 4.6- Strontium ferrite printed

The filament sample's magnetic remanence was highest when the sample was positioned perpendicular to the field, which is consistent with an easy axis in the filament radial direction and the model presented by Espinosa et al. on SF/PA12 filaments [16]. The angle dependence of the Mr is much smaller for the 3D printed sample and is almost absent in the 10 wt% 3D printed sample that shows an S slightly above 0.5. This differs from the result of Sapkota et al. on SF/PA12 3D printed samples [17], which show a significant magnetic anisotropy.

S-values, the ratio of Mr. Magnetic remanence, and Magnetization saturation were observed to evaluate anisotropic properties; they signify the easy and hard axis in produced Filament and printed samples, as shown in figure [8]. S values are directly proportional to Magnetic remanence; the highest S values are observed at 90 and 270-degree angles, and this suggests that the easy axis is perpendicular to the extrusion direction, which is consonant with previous studies [14,16,17]. There is a decrease in the S values curve in the printed samples, which could be attributed to the low shear flow in the extrusion channel of the 3D printers. Our results demonstrate a similar trend to Khadka et al. [20], showing that in magnetic composites, the S value remains relatively unchanged as the packing fraction of filler material ranges from 10wt% to 35wt%.



(a)



(b)

Figure 8 - (a) S Values 10 wt. % SFO filament and printed. (b) S Values 30 wt. % SFO filament and printed.

5.0 Conclusion

Polyamide 4.6 Strontium ferrite bonded magnetic composites were produced by extrusion technology in a 3d printable filament shape and then printed on a modified high-temperature 3D printer. It was observed that changes in flow rate and print temperature could help print high-performance polymer composites; filament and printed samples were compared and evaluated through morphological studies. Magnetic performance hysteresis loops were obtained using a vibrating sample magnetometer (VSM) to study the effects of high temperature 3d printing on magnetic composites of different packing fractions. It was observed that the produced filament composite exhibits variations in remanence magnetization with field angle. This reduction can be attributed to the alignment of the strontium ferrite particles during the printing process due to the shear flow effect in the extrusion channels.

Despite the high printing temperatures, the coercivity of the magnetic material remained unaffected due to the high-performance thermoplastic matrix. Magnetic anisotropy was evaluated from the obtained S-values, exhibiting that the material retained its anisotropic characteristics, retaining its easy and hard axis, which suggests it can be utilized to print functional anisotropic bonded magnets. Further research can explore areas such as the 3D printing of magnetic particles under the influence of external magnetic fields. The magnetic properties of printed bonded magnets under elevated temperatures can be explored to understand applications of bonded magnetic composite at elevated temperatures.

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6.0 Acknowledgment

This research was in-part funded by the National Science Foundation (NSF) under the DMR-MRI program, award number 2216440, and additionally supported by Texas State University's research Thesis Support fellowship. The authors thank Rahul Sheley and other Shared Research Operations (ARSC) staff at Texas State University for their technical guidance on materials characterization during the experimentation of this research and the Advanced Composite Lab at Texas State University's Ingram School of Engineering for providing the necessary equipment.

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