Recycled Sm-Co Bonded Magnet Filaments for 3D Printing of Magnets

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Abstract:
Recycling of rare earth elements, such as Sm and Nd, is one technique towards mitigating long-term supply and cost concerns for these materials. In this work recycled Sm-Co powder recovered from industrial grinding swarfs, or waste material from magnet processing, was investigated for use in preparation of filament for 3D printing of bonded magnets. Magnetic properties of the recycled Sm-Co powder recovered from swarfs were improved by blending in polylactic acid (PLA). Up to 30 vol.% of the recycled Sm-Co in PLA was extruded at 160˚C to produce a filament. It was demonstrated that no degradation of magnetic properties occurred due to the preparation or extrusion of the bonded magnet material. Good uniformity of the magnetic properties is exhibited throughout the filament, with the material first extruded being the exception. The material does exhibit some anisotropy, allowing for the possibility of magnetic alignment of particles. This work provides a path forward for producing recycled magnetic filament for 3D printing of permanent magnets.

Keywords: 3D printing, bonded magnets, recycling, Sm-Co

1. INTRODUCTION
Rare earth elements (REEs) like Sm and Nd provide the high energy product in permanent magnets necessary for many applications like hard-disk drives and electric vehicles. Long-term supply and cost of critical REEs like Nd are potential concerns for the magnet industry. Sm is not currently considered critical in terms of supply; however, supply disruption is likely to occur with the deployment of any technology with significant dependence on permanent magnets. Research efforts on addressing critical materials seek to provide solutions through materials conservation, recycling, and investigating alternative materials. Reuse of recycled magnets as powders in bonded magnets is one path towards materials conservation and recycling of critical REEs. By recycling magnet powder recovered from industrial grinding swarfs, the materials can be reclaimed via incorporation into bonded magnet fabrication. Swarfs are waste magnetic material generated from post-manufacturing of sintered magnets.

Bonded magnets, in which magnet powder is blended in a polymer binder, can be produced as near net-shape magnets without the need for extra manufacturing steps [1]–[3]. This conserves materials by minimizing wastes and reducing the energy required for manufacturing. Bonded magnets are typically manufactured by injection molding, calendering, extrusion, and compression molding [1], [3]. These techniques allow for manufacturing of complicated magnet geometries while achieving up to 70 (injection molding and calendering), 75, and 80 vol.% loading of magnet powder in binder respectively [1].

Additive manufacturing is a fast-emerging technique for bonded magnets [4]–[6]. Additive manufacturing techniques such as 3D printing have the potential advantage to reduce manufacturing costs by eliminating the need for mold fabrication. 3D printed bonded magnets with 54 to 65 vol.% loading of magnet powder in binder has been reported [5], [7]. Additively manufactured magnets with

65 vol.% loading of magnet powder in binder are able to outperform injection molded magnets, even at this early stage of the technique [7][4].

In this paper, we describe the preparation of permanent magnet filaments intended for 3D printing using bonded Sm-Co powder reclaimed from swarfs, in polylactic acid (PLA). Up to 30 vol.% loading of recycled Sm-Co powder in PLA is achieved in the extruded filament without degradation of magnetic properties.

2. METHODOLOGY

A. Material preparation

Recycled Sm-Co powder, recovered from swarfs, was loaded in polylactic acid (PLA). Two powders reclaimed from separate batches of industrial swarfs were used, denoted Sm-Co: A and Sm-Co: B. The PLA was first dissolved in solvent (methylene chloride) to obtain a viscous solution, aided by a mechanical homogenization at 14,000 rpm. The recycled Sm-Co powder was then dispersed in the viscous solution while still being homogenized. The solvent was evaporated at ~40°C while stirring with the homogenizer set to between 3,500 and 8,000 rpm to ensure the Sm-Co particles remained dispersed in the binder. For the first batch, Sm-Co: A powder was loaded in PLA at 5, 10, and 20 vol.%. After depleting the first batch of industrial swarf, the second batch, Sm-Co: B powder was loaded in PLA at 30 and 40 vol.%.

B. Extrusion

To extrude the permanent magnet filaments, the bonded Sm-Co/PLA material was cut into small pieces before and loaded into a filament extruder chamber. The chamber was inserted in the screw assembly, which was wrapped with heating tape set to 160˚C. A thermocouple was used to track the temperature of the heating tape and extruder. An allen wrench was used to push the heated material through a 0.4 mm diameter nozzle to extrude the filament.

C. Characterization

Scanning electron microscopy (SEM) was used to determine the initial particle size of each power. Elemental mapping was performed using X-ray fluorescence (XRF) to characterize the composition of both recycled Sm-Co powders. X-ray diffraction (XRD) was used to determine which phases of Sm-Co were present in each recycled Sm-Co powder. Differential scanning calorimetry was used to characterize the thermal properties of the PLA, powder, and bonded magnet material before and after extrusion.

Magnetic hysteresis plots were measured with a vibrating sample magnetometer at 300 K with the applied magnetic field varied from -3 T to 3 T. Each prepared material was measured before and after extrusion. Magnetic field was applied along the lengths of all extruded samples during magnetization measurements.

The uniformity of the extruded magnetic filament was determined by segmenting an extruded filament into seven parts of 3 mm length each, and measuring the magnetic hysteresis of each of the segments. The magnetic hysteresis loops of each sample was then compared with the hysteresis loop obtained by measuring the seven samples together. For all measurements, magnetic field was applied along the lengths of the samples.

III. RESULTS & DISCUSSION

A. Sm-Co: A Powder

The magnetic properties of the recycled Sm-Co: A powder (Fig. 1a) were compared to that of the properties of the powder loaded in PLA (Fig. 1b). The overall magnetic hysteresis loop shape improves

when the powder is loaded in the polymer for all loading fractions investigated. At low volume fractions of magnet powder in binder, the dipolar interaction between magnetic particles is minimized since the particles are separated; which likely accounts for the improved loop shape obtained when the Sm-Co powders were bonded in PLA, compared to the original powder.
The initial particle size and shape of the Sm-Co: A powder was characterized by SEM as depicted in Fig. 2a. The elemental composition of the Sm-Co: A powder was determined by XRF to be 18.35% Sm, 81.44% Co, and 0.22% Nd by atomic weight. The theoretical density was determined to be 8.34 g/cc from the elemental composition. The XRD peaks of the Sm-Co: A powder indicate that both Sm-Co 1:5 and 2:17 are present in the powder (Fig. 2b).

Up to 20 vol.% of Sm-Co: A powder in PLA was successfully extruded. Higher loading fractions were not investigated due to depletion of powder recovered from industrial swarfs. For the extruded samples (Fig. 1c), the coercivity and remanence were within 10% of unextruded material (Fig. 1b). Thus, the heating and extrusion did not result in significant degradation of the magnetic properties.

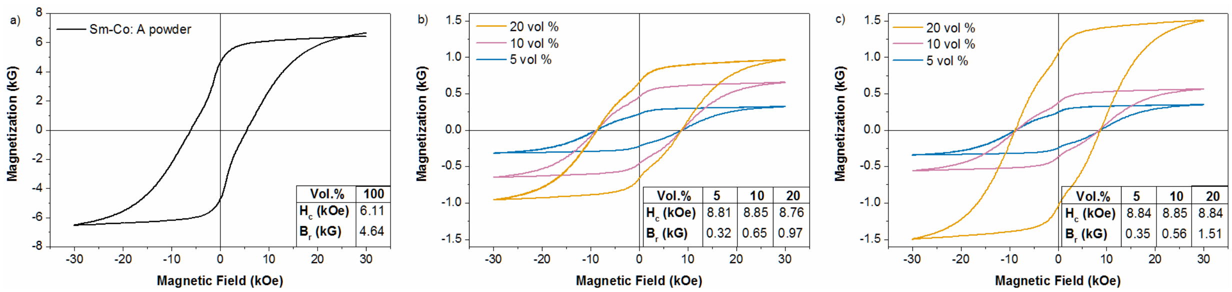

Fig. 1. Magnetic hysteresis of a) reycled Sm-Co: A powder, b) Sm-Co: A powder loaded in PLA at 5, 10, and 20 vol.%, before extrusion and c) Sm-Co: A powder loaded in PLA at 5, 10, and 20 vol.% after extrusion.

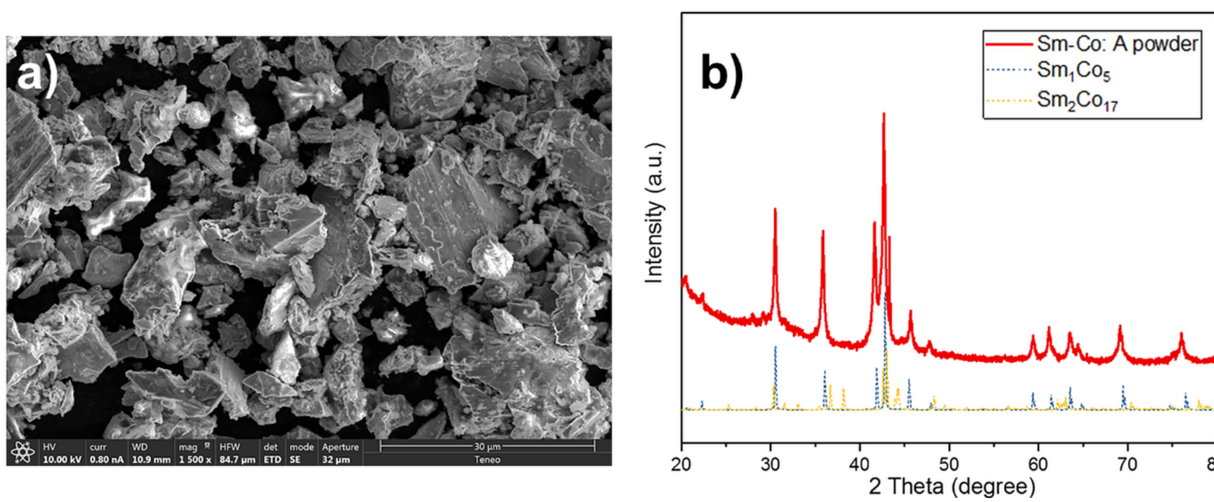

Fig. 2. a) SEM of Sm-Co: A powder and b) XRD of Sm-Co: A powder compared to reference cases of Sm-Co 1:5 and 2:17.

Fig. 3 shows the verification of the uniformity of the magnetic properties of the extruded filament. The coercivity and remanence both had a standard deviation less than 2% from the mean, indicating good uniformity of magnetic properties, which is also apparent from the magnetic hyestersis in Fig. 3. The only outlier is the first piece of extruded filament. It is possible that smallest particles were extruded first, giving a smaller particle size distribution than the rest of the filament, or that less particles were contained in the first extruded portion of the filament.

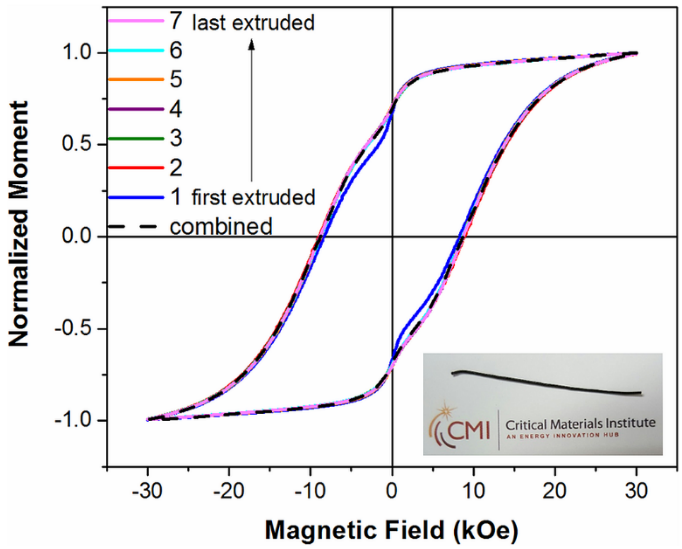

Fig. 3. Magnetic hysteresis of the 20 vol.% Sm-Co: A in PLA filament: 3 mm sections and all sections combined.

The Sm-Co: A powder does exhibit anisotropy. The magnetic hysteresis of the Sm-Co: A powder dispersed in epoxy was measured before and after applying a magnetic field of 3 T at 400 K. Some particle rotation likely occurred, improving the remanence and coercivity of the Sm-Co: A powder. This indicates that the magnetic properties of the extruded bonded magnetic filaments can be improved by an applied magnetic field.

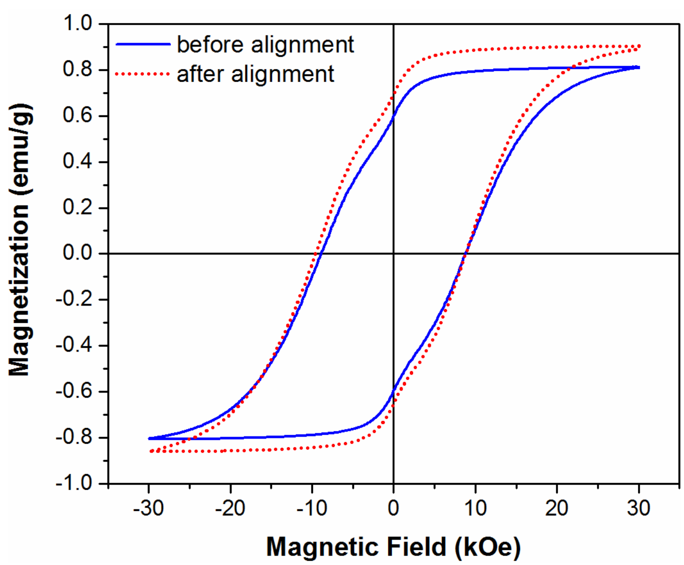

Fig. 4. Magnetic hysteresis of Sm-Co: A powder in epoxy measured at 300 K before and after alignment at 400 K under applied magnetic field of 3 T.

B. Sm-Co: B Powder

Sm-Co: B powder was recovered from a second batch of industrial swarfs after the first batch (Sm-Co: A powder) was depleted. The magnetic properties of the Sm-Co: B powder (Fig. 5a) were compared to that of the powder loaded in PLA at 30 and 40 vol.% (Fig. 5b). Higher loading fractions were used to investigate the limits of loading and extruding recycled magnet powder in PLA using the methodology described above.

Again, the magnetic hysteresis loop shape of the recycled Sm-Co powder was observed to improve by loading in PLA. At low volume fractions, the dipolar interaction between magnetic particles is minimized, likely accounting for improved magnetic properties. The initial particle size and shape of the Sm-Co: B powder were characterized by SEM as depicted in Fig. 6a. The XRD peaks of the Sm-Co: B powder indicate that both Sm-Co 1:5 and 2:17 are present in the powder (Fig. 6b). It has been reported that the increased percentage of Sm-Co 2:17 phase in Sm-Co magnets reduced coercivity [8]. Furthermore, the peaks indicate the presence of an oxide phase. The presence of a soft magnetic phase likely accounts for the poor magnetic hysteresis loop shape of the powder. This is bolstered from the elemental composition of the Sm-Co: B powder, which was determined to be 11.64% Sm, 53.60% Co, 3.94% Cu, 2.25% Zr, 0.18% Nd, and **28.38% Fe** by atomic weight. The theoretical density was determined to be 8.19 g/cc from the elemental composition. It has been reported by [9] and [10] that Fe containing soft phase in Sm-Co reduces the coercivity.

30 vol.% Sm-Co: B powder was successfully extruded using the process described above. Extrusion of 40 vol.% Sm-Co in PLA was not possible using the described methodology and is likely due to the small nozzle size and lack of sufficient force to push material through the nozzle. For the extruded sample (Fig. 5c), the coercivity and remanence were within 10% of unextruded material (Fig. 5b). Thus, the heating and extrusion did not result in significant degradation of the magnetic properties.

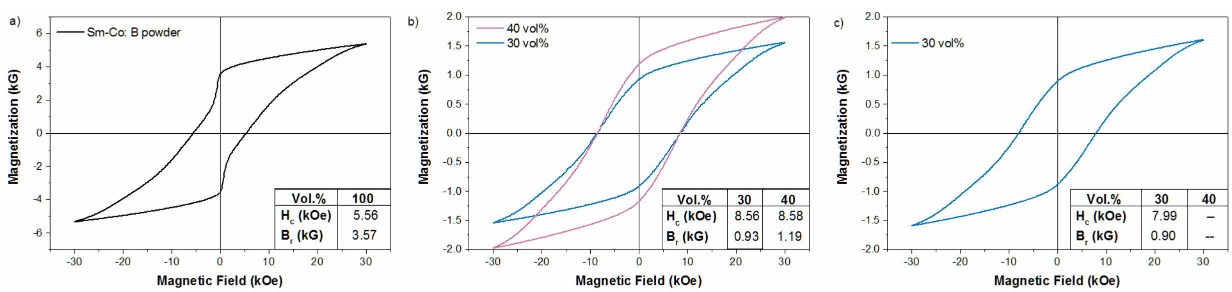

Fig. 5. Magnetic hysteresis of a) reycled Sm-Co: B powder, b) Sm-Co: A powder loaded in PLA at 30 and 40 vol.%, before extrusion and c) Sm-Co: A powder loaded in PLA at 30 vol.% after extrusion.

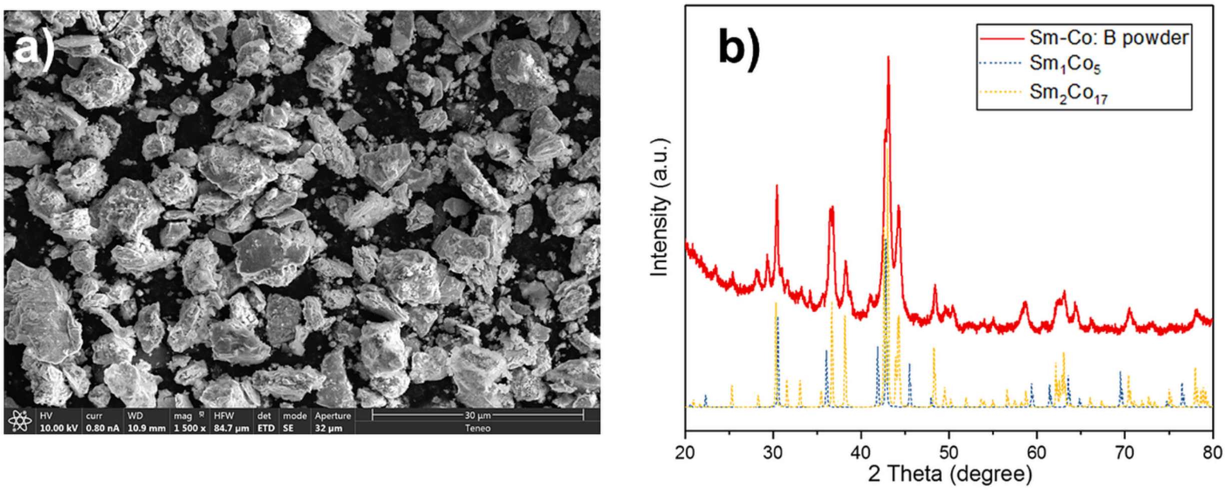

Fig. 6. a) SEM of Sm-Co: A powder and b) XRD of Sm-Co: A powder compared to reference cases of Sm-Co 1:5 and 2:17.

IV. CONCLUSIONS

Bonded magnet filaments were prepared by extrusion of recycled Sm-Co powder in PLA with up to 30 vol.% loading of magnet powder in binder. It was demonstrated that loading recycled Sm-Co powder in polymer improved the magnetic properties, likely due to minimized dipolar interaction at low volume fractions of magnet powder. No significant degradation of magnetic properties occurred due to the extrusion process. Furthermore, good uniformity of the magnet filament was demonstrated. In future work, higher loading fractions will be investigated using more powerful extrusion techniques, and plasticizers will be added to the filament to allow for 3D printing of recycled bonded magnets.

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REFERENCES

[1] J. Ormerod, S. Constantinides, J. Ormerod, and S. Constantinides, “Bonded permanent magnets : Current status and future opportunities,” *J. Appl. Phys.*, vol. 81, pp. 4816–4820, 1997.

[2] B. M. Ma, J. W. Herchenroeder, B. Smith, M. Suda, D. N. Brown, and Z. Chen, “Recent development in bonded NdFeB magnets,” *J. Magn. Magn. Mater.*, vol. 239, pp. 418–423, 2002.

[3] J. J. Croat, “Current status and future outlook for bonded neodymium permanent magnets (invited),” *J. Appl. Phys.*, vol. 81, no. 8, pp. 4804–4809, 1997.

[4] L. Li, A. Tirado, I. C. Nlebedim, O. Rios, B. Post, V. Kunc, R. R. Lowden, E. Lara-curzio, R. Fredette, J. Ormerod, T. A. Lograsso, and M. P. Paranthaman, “Big Area Additive Manufacturing of High Performance Bonded NdFeB Magnets,” *Sci. Rep.*, vol. 6, pp. 1–7, 2016.

[5] C. Huber, C. Abert, F. Bruckner, M. Groenefeld, O. Muthsam, S. Schuschnigg, C. Vogler, R. Windl, and D. Suess, “3D print of polymer bonded rare-earth magnets , and 3D magnetic field scanning with an end-user 3D printer,” *Appl. Phys. Lett.*, vol. 109, p. 162401, 2016.

[6] J. Ja cimovi c, F. Binda, L. G. Herrmann, F. Greuter, J. Genta, M. Calvo, T. Tomse, and R. A. Simon, “Net Shape 3D Printed NdFeB Permanent Magnet,” *Adv. Eng. Mater.*, p. 1700098, 2017.

[7] L. Li, B. Post, V. Kunc, A. M. Elliott, and M. P. Paranthaman, “Additive manufacturing of near-net-shape bonded magnets : Prospects and challenges,” *Scr. Mater.*, vol. 135, pp. 100–104, 2017.

[8] C. Yang, L. Jia, S. Wang, C. Gao, D. Shi, Y. Hou, and S. Gao, "Single Domain SmCo5@Co Exchange-coupled Magnets Prepared from Core/shell Sm[Co(CN)6].4H20@GO Particles: A Novel Chemical Approach," *Sci. Rep.*, vol. 3, no. 3542, pp. 1–7, 2013.

[9] B. Shen, A. Mendoza-Garcia, S. E. Baker, S. K. Mccall, C. Yu, L. Wu, and S. Sun, "Stabilizing Fe Nanoparticles in the SmCo 5 Matrix," *Nano Lett.*, vol. 17, pp. 5695–5698, 2017.

[10] P. Saravanan, M. Premkumar, A. K. Singh, R. Gopalan, and V. Chandrasekaran, "Study on morphology and magnetic behavior of SmCo 5 and SmCo 5 / Fe nanoparticles synthesized by surfactant-assisted ball milling," *J. Alloys Compd.*, vol. 480, pp. 645–649, 2009.