

Challenges in postprocessing of hybrid manufacturing of magnet polymer composites to enhance the energy product of NdFeB bonded magnets

Tej Nath Lamichhane^{1*}, Kaustubh Mungale^{2,3,4}, Haobo Wang^{1,5}, Kinjal Gandha⁶, Xubo Liu⁶, Ikenna C. Nlebedim⁶, Zhang Gai⁷, Uday Kumar Vaidya^{2,3,4} and M. Parans Paranthaman^{1**}

¹*Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

²*Tickle College of Engineering, The University of Tennessee, Middle Drive, Knoxville, TN 37996, USA*

³*Manufacturing Sciences Division, Oak Ridge National Laboratory, 2350 Cherahala Blvd, Knoxville, TN 37932, USA*

⁴*Institute for Advanced Composites Manufacturing Innovation, 2360 Cherahala Blvd, Knoxville, TN 37932, USA*

⁵*The Bredesen Center, The University of Tennessee, Knoxville, TN 37996, USA*

⁶*Critical Materials Institute, Ames Laboratory, Ames, IA 50011, USA*

⁷*Center for Nanophase Materials Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

Abstract:

Bonded permanent magnets need to process magnet particles and fillers together which is a form of hybrid or composite manufacturing that needs to simultaneously process multimaterials. Polymer bonding of the permanent magnets decreases the energy product of the bonded magnets which varies with square of loading fraction of magnetic materials. However, due to high viscosity of bonding polymer prohibits loading higher than 80 volume % of magnetic materials in most efficient loading process such as compression molding. To further increase the loading of magnetic fraction in the bonded permanent magnets, it is expected to be beneficial to introduce a fraction of nonreacting thermally sacrificial polymer along with permanent bonding polymer in the least permissible of about 20 volume % of the polymer. [This process of first adding the sacrificial polymer for higher processability for composites and later removing it via heat treatment provides a simple example of inclusion of both the additive and the subtractive stages of hybrid manufacturing.](#) These hybrid composite magnets can be heat treated to remove the sacrificial

polymer to further increase the density and energy product which might require to implement hot isostatic pressing. Although the identification of such ideal polymer requires an excessive polymer chemistry research, we have compression molded several permanent bonding polymers such as nylon, polycarbonate (PC) and polyphenyl sulfide (PPS) and potential sacrificial polymer such as polyoxymethylene (POM), polystyrene (PS), and Acrylonitrile Butadiene Styrene (ABS). and it is discovered that oxygen free low temperature pyrolyzable polymers could be the potential candidates for increasing the magnet particles loading for achieving high energy products.

*lamichhanetn@ornl.gov, **paranthamanm@ornl.gov

Introduction

Hybrid manufacturing process encompasses combination of multiple processing techniques as well as simultaneous processing of multimaterials to improve the overall quality of the process and products¹. Permanent magnets energy product boosting is a critical manufacturing challenge both in sintered magnets and bonded magnets. Most powerful grade of magnets are traditionally sintered magnets which require several conventional processing steps such as powder metallurgy², strip casting³, and complex thermal treatment cycles. These complex manufacturing steps makes the permanent magnets coprocessing with other electrical machines components such as magnet holder rotor core very complicated if not impossible. Broadly speaking, the electrical machines in this article refers to motors, generators, power electronics and additional devices that incorporates soft magnets, permanent magnets, electrical conductors, cooling channels and sensors. In bonded magnets, there are several well-established techniques such as compression molding, injection molding, calendaring and extrusion⁴ which can be categorized as hybrid or semihybrid manufacturing technique since the magnetic filers need to be blended with binders and coprocessed to manufacture the magnets. The extrusion based bonded magnets manufacturing technique is emerging as additive manufacturing also known as 3D printing technique such as fused deposition modeling where the magnets composites can be printed in complex shapes^{5,6}. Bonded magnets are very important to reduce the eddy current loss, increase the flexural strength and complex shapes and sizes moldability⁷.

There are very few hybrid magnets manufactured literature reports mainly in form of 3D printing of two types of powders and binders. Yang et al. 3D printed the mixture of anisotropic NdFeB and SrFe₁₂O₁₉ powder using epoxy extrusion technique and magnet density of 3.78 – 3.64 g/cc

depending upon content of mixed ferrite powder⁸. Similarly, Gandha et al. used the fused deposition modeling based big area additive manufacturing of anisotropic NdFeB and Sm-Fe-N powder in nylon binder and heat treated in external magnetic field to generate up to 11 MGOe energy product⁹. There are not many initiatives of removal of some nonmagnetic fragments of binder from post processing such as heat treatment and consolidation at the end of hot isostatic pressing is not pursued as an avenue to enhance the energy product of the fabricated magnets. Rather the energy product of the bonded magnets is greatly reduced due to inclusion of nonmagnetic binders where energy product varies as the square of the filling fraction. In the current most efficient filling method, compression molding can process up to 80 volume %¹⁰ of magnetic filler in the commercial binders, in general permanent, such as nylon, polyphenylene sulfide and polycarbonates. An 80 volume % magnetic fillers packing cannot provide more than 64% of the energy product of the starting magnetic powder which could be up to 25 MGOe for the 40 MGOe anisotropic precursor powders. However, to further increase the energy product of the bonded magnets, there is need to develop a new method of increasing the volume fraction of the magnetic fillers which is already optimized for most of the commercial magnetic binders.

Hybrid manufacturing with integrated multimaterials processing of additive manufacturing technologies and subtractive modes of parts accessing, surface treatments, tolerance maintenance and postprocessing capabilities would be the next steps towards next generation of electrical machines production. Such hybrid production units would be very essential for the onsite production and installation of large high performance electrical machines such as wind turbines. Since the high-performance electrical machines needs high energy product sintered magnets, it is essential to increase the energy product of the bonded magnets to make them more applicable. Large electrical machines and their components are inherently complicated to manufacture due to

their component's wise complex materials composition as well as gigantic structures. Hybrid manufacturing of electrical machines is essential for the next generation of electrical machines which includes onsite manufacturing, installation and boosting the overall performance¹¹. Recently General Electric and Company has announced the additive manufacturing of nacelle and additional large metallic components of wind turbines which also includes sand/ceramics ink jetting for the molds fabrication¹². One of the biggest challenges of a single-attempt-built electrical machines would be simultaneous processing of soft magnetic materials for electrical cores, permanent magnets, winding electrical conductors and insulating materials due to their very dissimilar materials processing techniques and thermal cycles. Being the key component of electrical machines, investigation about the possibility of coprocessing of permanent magnets in hybrid manufacturing of electrical machines is essential. Due to very high temperature thermal processing cycles of soft magnets and electric conductors in comparison to permanent magnets, a low temperature thermal processing at the final stage of the hybrid manufacturing process is essential for permanent magnets. An intuitive approach could be to come up with stepwise processing of multimaterials components for the electrical machines such as casting of soft laminates separated by thin, soft magnetic insulator laminates¹¹, casting/printing of unconventional conducting cables^{13,14}, cooling channels followed by permanent magnets to achieve the single built electrical machine. Among these steps, permanent magnets are the most expensive part of the electrical machines and cannot be easily casted in a large shape and size and properly magnetized in desired direction. This is due to the requirement of complex thermal cycles for the magnets microstructure refinement to achieve their monomagnetic domain sizes, their alignment and magnetization to achieve the permanency specially in fully sintered magnets. In such a scenario, bonded permanent magnets still could be processed via either inkjetting of soft magnetic phase for the preoptimized

monodomain magnetic particles or extruding the magnet polymer composite in the designated slots for the permanent magnets. However, low eddy current loss is a very important factor for achieving higher efficiency in electrical machines and requires thin laminates of soft magnetic materials. Similarly in bonded permanent magnets, the eddy current could be greatly reduced since the polymer binding greatly increases the electrical resistance and loss fraction of magnetization⁷. One of the options could be to compress molding large permanent magnets sections in a soft steel enclosure, heat treat and enhance the energy product via partial removal of nonmagnetic mostly sacrificial binder and high temperature isostatic pressing, and hermetically seal and magnetize them before they are installed in the ceramics casted slots of electrical rotors.

To exceed the current loading fraction of magnetic particles and reap the benefits of lower eddy current in bonded magnets, we investigate the opportunities and challenges of hybrid manufacturing of bonded magnets with permanent and sacrificial binder polymers with maximum particles loading (e.g. 80 volume % of NdFeB) using compression molding and post processing. The key task was to fabricate the bonded NdFeB magnets with two types of binder and heat treat to remove the low temperature melting “hereby sacrificial polymer” to increase the overall density of the bonded magnets. To successfully execute this idea, the biggest challenge starts from identification of possible sacrificial binder that does not react with high melting temperature commercial binder polymer “hereby permanent polymer” while heat treating and does not degrade the magnet properties during low temperature pyrolysis. We selected the easily available low melting polymers both oxygenated and oxygen free polymers as sacrificial binders, compressed molded with permanent binders such as nylon, polyphenylene sulphide and polycarbonates and postprocessed. The preliminary study revealed that oxygen free low temperature pyrolyzable

polymers that do not react with permanent binders and do not degrade the magnetic particles would be the ideal candidates to be discovered in future.

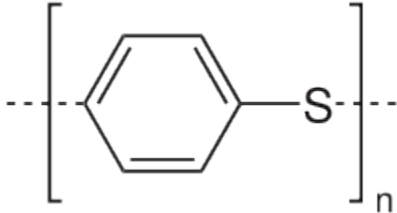
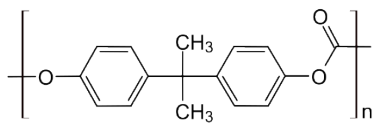
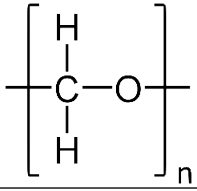
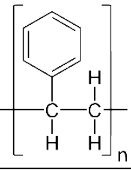
Method

As permanent binders, relatively higher melting temperature with well-established processing techniques such as nylons, polyphenylene sulfide (PPS), and polycarbonates (PC) were selected. As potential sacrificial polymers low melting temperature polymers (polyoxymethylene (POM), polystyrene (PS) and acrylonitrile butadiene styrene (ABS) were selected (chemical formula and melting temperatures are reported in Table 1). Anisotropic Magnequench magnet powders were used for the compression molding. The process of the compression molding of the composite is reported elsewhere¹⁵. Heat treatment of the composites to remove the sacrificial polymers were carried out under the Ar flow environment both with and without magnetic field up to 10 hours. The magnetic properties of the samples were measured Quantum Design Dynacool magnetometer with a magnetic field of up to $\mu_0 H = 9$ T.

Results and discussion

In case of sacrificial polymer with oxygen, the magnetic coercivities of the heat-treated samples were almost completely lost. As a representative result, PC bonded magnet compounded with POM showed significant loss of coercivity after heat treatment at 600 °C to remove all the weight of sacrificial polymer POM compared with as-compounded sample (Fig. 1). Additionally, the mechanical properties of the sample were degraded significantly. This outcome suggests that the sacrificial polymer removal should be executed in relatively low temperature. Another parameter is the time of heat treatment so that coercivity of the magnet is also not degraded in addition to mechanical properties. Ultimately, to achieve the dense magnet, hot isostatic pressing will be essential to increase the overall density of the magnet¹⁶.

Table 1. Description of trailed polymers. Top three are permanent and lower three are considered sacrificial.

Polymers	Formula	Melting temperature (°C)	Remarks
Polyphenylene sulphide		~280	Oxygen free permanent polymer
Nylon	$(C_{12}H_{22}N_2O_2)_n$	268.8	Oxygen containing permanent
Polycarbonate		288-316	Oxygen containing permanent
Polyoxymethylene		175	Oxygen containing sacrificial
Polystyrene		270	Oxygen free sacrificial
Acrylonitrile Butadiene Styrene (ABS)	$(C_8H_8 \cdot C_4H_6 \cdot C_3H_3N)_n$	105	Oxygen free sacrificial

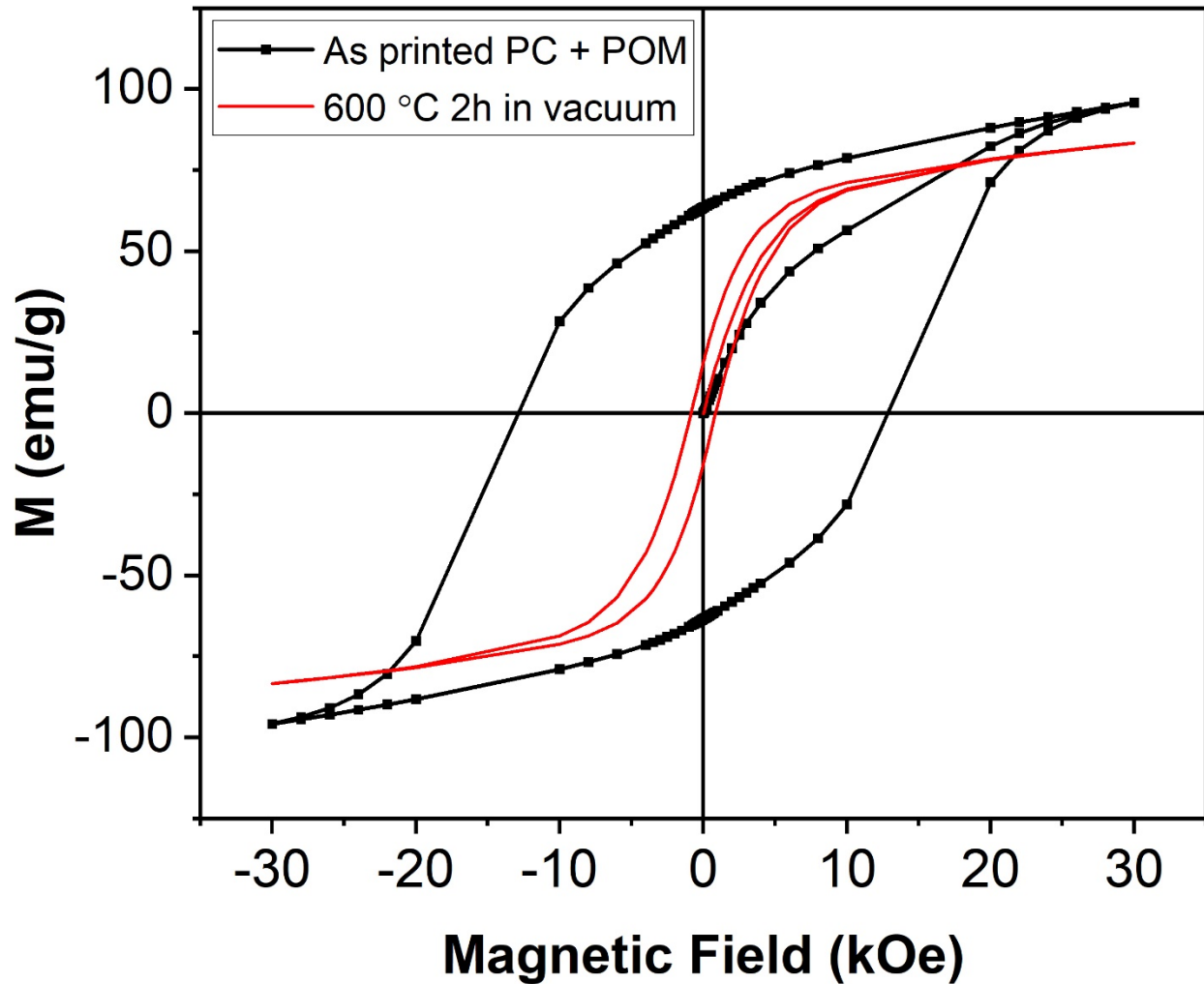


Figure 1: Room temperature magnetization of as compressed molded and 600 C 2 h heat treated polycarbonate and polyoxymethylene pairs up to weight percentage corresponding of sacrificial polymer.

Figure 2 shows the magnetic properties of the NdFeB, nylon and ABS compression molded magnets. Fig. 2(a) shows the room temperature magnetization of as printed and heat-treated samples in Ar atmosphere for 10 h which shows a significant (11.5 %) decrease in coercivity. Fig. 2 (b) shows the magnetization for the same batch in presence of the magnetic field at 300 °C and 350 °C temperatures. Corresponding coercivity, % mass loss of the samples and saturation magnetization are shown in Table 2. In comparison to coercivity, the saturation magnetization loss is negligible. As expected, preserving the coercivity is a crucial parameter in hybrid magnet

manufacturing as it is generating it in sintering technique. The most important outcome of the Nylon/ABS composite is that although nylon has oxygen in it, it does not degrade the magnets. There is almost comparable coercivity in the as printed sample for the sample which was heat treated under Ar flow for about 10 h as shown in in the inset of Fig. 2(b).

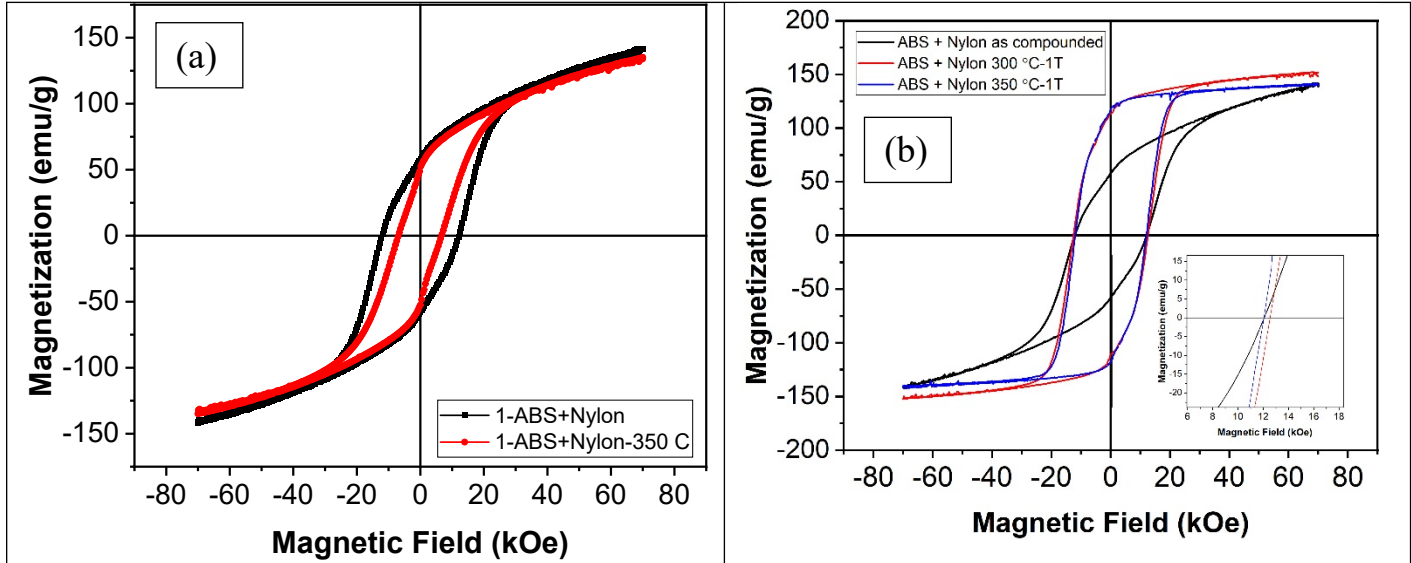


Figure 2: Comparison of magnetization of as compressed molded and heat treated NdFeB+ ABS + Nylon composite (a) without applied field (b) with applied field.

Table 2. Measurement of coercivities, % mass loss and saturation magnetization in the heat-treated ABS+Nylon NdFeB magnet composite.

Dataset ID	Coercivity (kOe)	Mass loss % of the sample	Saturation Magnetization (emu/g)
ABS+Nylon-300 C-2h-1T	12.2	0.32	154.0
ABS+Nylon-300 C-5h-1T	12.2	0.61	153.4
ABS+Nylon-300 C-10h-1T	10.8	0.81	151.4
ABS+Nylon as compounded	12.2	-	141

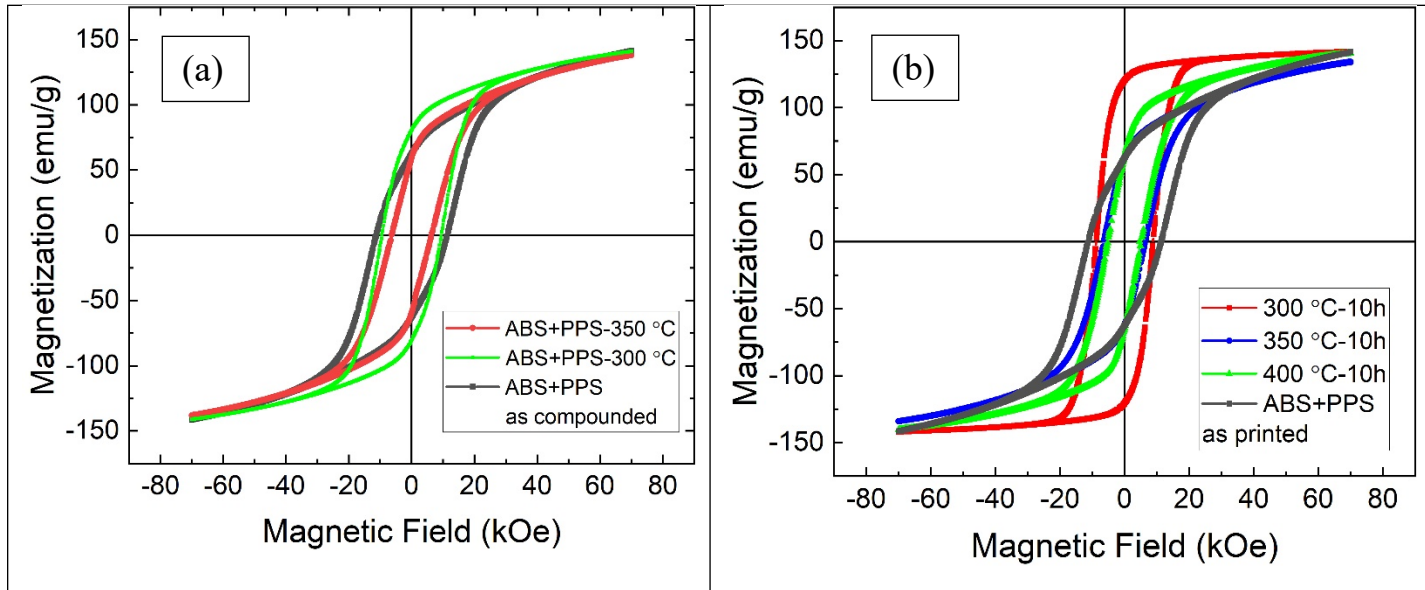


Figure 3: Comparison of magnetization of as compressed molded and heat treated NdFeB+PPS+ABS composite (a) without field (b) with applied field.

Figure 3 shows the comparison of magnetic hysteresis loops as compounded, and heat treated NdFeB/PPS/ABS composite samples without applied field in Fig. 3(a) and with applied magnetic field in Fig. 3(b). The coercivities, mass loss % and saturation magnetizations are presented in Table 3. The coercivity of the heat treated NdFeB PPS/ABS composite samples are drastically decreasing despite no oxygen both in PPS and ABS.

Table 3. Measurement of coercivities, % mass loss and saturation magnetization in the heat-treated ABS/PPS NdFeB magnet composite.

Dataset ID	Coercivity (kOe)	Mass loss % of the sample	Saturation Magnetization (emu/g)
ABS + PPS as compounded	11.4	-	141.6
ABS + PPS -300 °C-1T	9.4	0.4	141.9

ABS + PPS -350 °C-1T	6.19	0.5	138.2
ABS + PPS -400 °C-1T	5.1	1.48	141

From the experimental evidence of compression molding of NdFeB, low melting temperature and oxygen-free sacrificial polymers like ABS is a promising candidate. In case of oxygenated and oxygen free permanent polymer, it is not clear whether oxygen from those permanent polymers is detrimental below melting temperature of permanent polymer or not. In fact, the role of oxygen constituent in polymer binders for bonded magnets was not previously reported. As the hybrid manufacturing is getting unprecedented attention, and permanent magnet is the key component of the electrical machines, it is crucial to find a proper way of coprocessing of permanent magnets designing as well as enhancing the energy produce after initial manufacturing. In this regards, low temperature processing techniques such as compressing molding, fused deposition modeling, binder jetting etc. can be combined to already casted/printed soft magnetic rotor slots without alternating the mechanical and magnetic properties of the soft magnetic materials. As the post processing of ABS/Nylon shows very encouraging result although we just tested few pairs of polymers. As this research will progress, there needs to identify appropriate pair of polymers to remove a sacrificial polymer without sacrificing the magnetic properties. The future area to focus could be identifying low temperature, low heat treatment time and easy hot isostatic pressing technique to increase the density of the permanent magnets.

Conclusions

The preliminary concept of hybrid manufacturing of NdFeB bonded magnets various permanent commercial binders such as polycarbonate, nylon, and PPS mixed with various low melting

polymers with and without constituent oxygen. The Nylon /ABS binder pairs preserve the magnetic properties almost intact among the tested pairs up to 10 h heat-treatment under inert atmosphere although much high temperature heat treatment is essential to completely remove the sacrificial components. These preliminary results highlight the area to focus on identifying low temperature, oxygen free pyrolyzable sacrificial polymer along with easily processable permanent binder such as nylon.

ACKNOWLEDGEMENT

This research was supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office.

This manuscript has been authored by UT-Battelle, LLC, under contract DE-AC05-00OR22725 with the US Department of Energy (DOE). The US government retains and the publisher, by accepting the article for publication, acknowledges that the US government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US government purposes. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

References

1. Zhu Z, Dhokia VG, Nassehi A, Newman ST. A review of hybrid manufacturing processes – state of the art and future perspectives. *Int J Comput Integr Manuf.* 2013;26(7):596-615. doi:10.1080/0951192X.2012.749530

2. Constantinides S. MANUFACTURE OF MODERN PERMANENT MAGNET MATERIALS. :12.
3. Kaneko Y, Kuniyoshi F, Ishigaki N. Proven technologies on high-performance Nd–Fe–B sintered magnets. *J Alloys Compd.* 2006;408-412:1344-1349. doi:10.1016/j.jallcom.2005.04.169
4. Staff E. Bonded Magnets: A Versatile Class of Permanent Magnets. *Magnetics Magazine*. Published July 7, 2015. Accessed October 10, 2021. <https://magneticsmag.com/bonded-magnets-a-versatile-class-of-permanent-magnets/>
5. Li L, Tirado A, Nlebedim IC, et al. Big Area Additive Manufacturing of High Performance Bonded NdFeB Magnets. *Sci Rep.* 2016;6(1):36212. doi:10.1038/srep36212
6. Li L, Post B, Kunc V, Elliott AM, Paranthaman MP. Additive manufacturing of near-net-shape bonded magnets: Prospects and challenges. *Scr Mater.* 2017;135:100-104. doi:10.1016/j.scriptamat.2016.12.035
7. Paranthaman MP, Yildirim V, Lamichhane TN, et al. Additive Manufacturing of Isotropic NdFeB PPS Bonded Permanent Magnets. *Materials.* 2020;13(15):3319. doi:10.3390/ma13153319
8. Yang F, Zhang X, Guo Z, Ye S, Sui Y, Volinsky AA. 3D printing of NdFeB bonded magnets with SrFe₁₂O₁₉ addition. *J Alloys Compd.* 2019;779:900-907. doi:10.1016/j.jallcom.2018.11.335
9. Gandha K, Li L, Nlebedim IC, et al. Additive manufacturing of anisotropic hybrid NdFeB-SmFeN nylon composite bonded magnets. *J Magn Magn Mater.* 2018;467:8-13. doi:10.1016/j.jmmm.2018.07.021
10. Ormerod J, Constantinides S. Bonded permanent magnets: Current status and future opportunities (invited). *J Appl Phys.* 1997;81(8):4816-4820. doi:10.1063/1.365471
11. Lamichhane TN, Sethuraman L, Dalagan A, Wang H, Keller J, Paranthaman MP. Additive manufacturing of soft magnets for electrical machines—a review. *Mater Today Phys.* 2020;15:100255. doi:10.1016/j.mtphys.2020.100255
12. GE & Co to Develop World’s Largest 3D Printer for Offshore Wind Application. *Offshore Wind*. Published September 21, 2021. Accessed September 26, 2021. <https://www.offshorewind.biz/2021/09/21/ge-co-to-develop-worlds-largest-3d-printer-for-offshore-wind-application/>
13. Yan Y, Ding C, Ngo KDT, Mei Y, Lu G-Q. Additive manufacturing of planar inductor for Power Electronics applications. In: *2016 International Symposium on 3D Power Electronics Integration and Manufacturing (3D-PEIM)*. ; 2016:1-16. doi:10.1109/3DPEIM.2016.7570536

14. Ding C, Lu S, Liu L, Ngo KDT, Lu G-Q. Additive Manufacturing of Hetero-Magnetic Coupled Inductors. *IEEE Trans Compon Packag Manuf Technol.* 2021;11(6):1028-1034. doi:10.1109/TCPMT.2021.3083179
15. Mungale K, Lamichhane TN, Wang H, Sales BC, Paranthaman MP, Vaidya UK. Compression molding of anisotropic NdFeB bonded magnets in a polycarbonate matrix. *Materialia.* 2021;19:101167. doi:10.1016/j.mtla.2021.101167
16. Sagawa M, Nagata H, Watanabe T, Itatani O. Rubber Isostatic Pressing (RIP) for Ferrite Magnets. *J Phys IV Proc.* 1997;07(C1):C1-307-C1-308. doi:10.1051/jp4:19971120