

Influence of filler surface treatments on processability and properties of polymer-bonded Nd–Fe–B magnets

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Polymer-bonded magnets composed of polymer matrices and magnetic fillers (hard ferrites of Ba and Sr systems, Alnico and rare earth magnetic systems such as SmCo_5 , $\text{Sm}_2(\text{Co, Fe, Cu, Zr})_{17}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloys) are produced by traditional methods of polymer processing and offer significant advantages, in terms of shaping and cost, over their metallic or ceramic counterparts [1, 2]. They are prepared by blending a magnetic filler with a polymeric binder in a mixer or extruder. The resulting composite material can be shaped into magnetic components with complex shapes by using conventional polymer processing methods such as injection molding.

Presently, the processability and applications of polymer-bonded magnets are limited because of their low energy product $(BH)_{\text{max}}$ and poor heat resistance properties [3–5]. Therefore, there is a need to develop polymer-bonded magnets with enhanced magnetic properties for high-temperature and aggressive environments. In this letter, we report progress on our research on surface modification of magnetic NdFeB fillers, synthesis and characterization of suitable magnetic rare earth alloy powders and polymer matrices. Gas-atomized spherical powders produced in-house by Ames Laboratory and commercial NdFeB powders manufactured by Magnequench were studied. The former was studied because of the free-flowing behavior and maximum packing fraction of spherical powders.

Thermal and rheological characterizations of the high-temperature polymers showed that poly (phenylene sulfide) (PPS) (RYTON P-6, Phillips Petroleum Company, Oklahoma, USA) was found to have the best combinations of properties for making polymer-bonded magnets for high-temperature and aggressive environments. Two other polymers, poly (ether sulfone) and poly (phenylene sulfone), were identified as potential polymer matrices for polymer-bonded magnets, but their high viscosity needs to be modified to allow the high-volume loading of the NdFeB powders required for maximal magnetic properties.

Testing of the pure magnetic powders showed that NdFeB (MQP-O, Magnequench International, Inc., Indiana, USA) had the right properties, such as high $(BH)_{\text{max}}$, for the targeted application. The morph-

ology of both the gas-atomized and MQP-O powders was studied using scanning electron microscopy (SEM). The results showed that the gas-atomized powder had particle sizes (mean particle size = $40 \mu\text{m}$) finer than that of the MQP-O powder (mean particle size = $200 \mu\text{m}$), indicating that the specific surface area per unit volume of gas-atomized powder is much larger than that of the MQP-O powder. The higher specific surface area is thought to increase the observed reactive tendency of the sample when heated in air at high temperatures. The observed lower $(BH)_{\text{max}}$ of the bonded magnet containing the gas-atomized powder can be partly ascribed to the reactivity (described later) of the powder during processing.

To understand the flow behavior of the NdFeB/PPS magnet, we measured rheological properties of the magnets at low concentrations of 2 to 15 vol% of NdFeB powder (coated and uncoated with silane coupling agents, as described later) in the PPS polymer binder using a mechanical spectrometer under dynamic oscillatory shear flows. The results confirmed our expectation of a reduction of the viscosity of the suspensions caused by the presence of the monolayer of the silane coupling agent on the surface of the powder (see Fig. 1). Further, the results showed that the particle size distribution of the powder has a major effect on the rheological property of the magnetic suspension, as depicted in Fig. 2. The effect of the silane coupling agent is partly believed to be due to good wetting of the magnetic powders, but a definitive statement of the exact mechanism cannot be made at this time. Morphological and chemical analysis data (not shown) support this interesting wetting phenomenon.

To assess the role of melting and crystallization behavior of the polymer binder on the processability of the polymer-bonded magnets, we used a differential scanning calorimeter to study the melting and crystallization behavior of the polymer. The results showed that these phase transitions of the polymer are little affected by the presence of the NdFeB powders (see Tables I and II and Fig. 3). It is likely that the silane coupling agent will affect the crystallization kinetics of the polymer in the presence of the magnetic powders. This is a matter for further investigation.

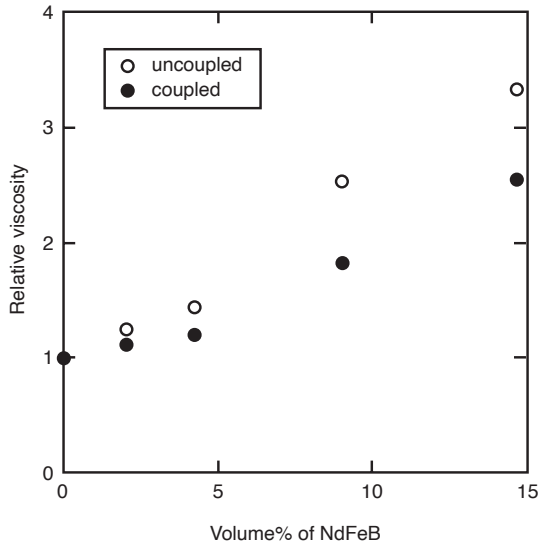


Figure 1 Effect of coupling agent on relative viscosity of PPS/NdFeB composite under oscillatory shear flow in the parallel plate configuration [100 rad/s, 290 °C; 10% strain].

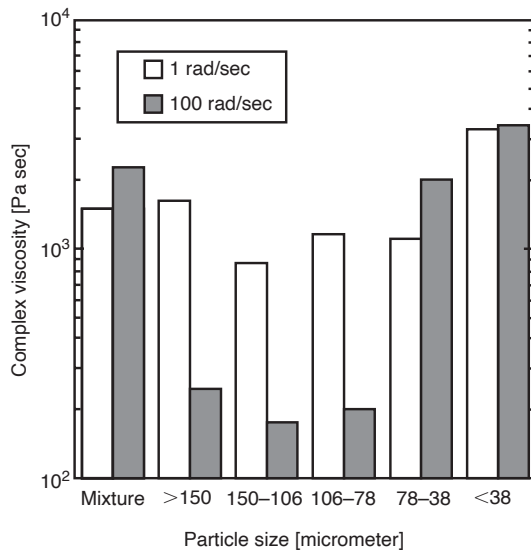


Figure 2 Effect of particle size of NdFeB powder on the complex viscosity of 85 vol% PPS/15 vol% NdFeB suspension under oscillatory shear flow in the parallel plate configuration ($\omega = 1$ and 100 rad/s, 290 °C; 10% strain).

TABLE I Normalized melting and crystallization peak areas of the PPS-bonded NdFeB sample

PPS/NdFeB wt%	Melting area (J/g)		Crystallization area (J/g)	
	Uncoupled	Coupled	Uncoupled	Coupled
100/0	46.519		49.680	
88/11	45.584	44.604	48.335	48.446
80/20	43.493	42.544	47.106	46.524
64/36	42.816	41.658	46.022	45.150
50/50	43.574	41.416	47.502	44.904

The research conducted thus far showed that the difficulties of processing polymer-bonded NdFeB magnets for high-temperature uses can be avoided by using silane coupling agents to coat the surface of the powders prior to incorporating them into the

TABLE II Melting and crystallization temperatures of PPS in the PPS-bonded NdFeB sample

PPS/NdFeB wt%	Melting temperature °C		Crystallization temperature °C	
	Uncoupled	Coupled	Uncoupled	Coupled
100/0	278.789		238.433	
88/11	278.787	277.785	239.262	236.433
80/20	277.638	277.966	237.756	237.923
64/36	276.950	276.990	237.415	236.255
50/50	276.460	276.466	235.918	235.907

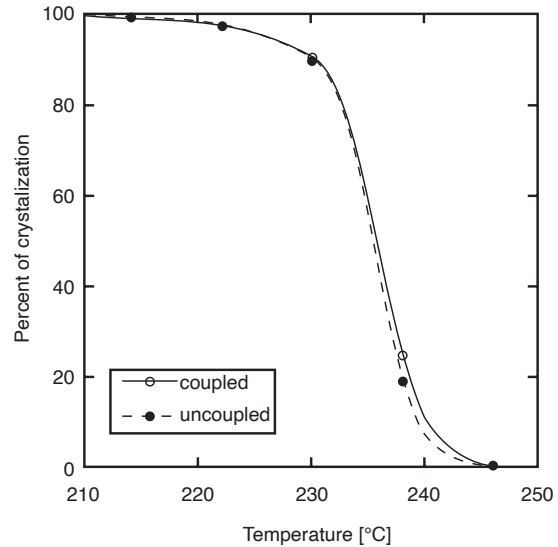


Figure 3 Effect of coupling agent on crystallization behavior of PPS polymer binder (cooling rate = 10 °C/min).

polymer matrix. Silane coupling agents are known to improve particulate filler dispersion in continuous polymer matrices, allowing increased loading of the fillers without increasing bulk viscosities of the composite [6, 7]. The silane coupling agent was applied by simple immersion in the desired concentration of aqueous solution of the silane (approximately 1% aqueous silane solution). After immersion for about 5 min, the excess silane solution was decanted and the powders were dried to constant weight in a vacuum oven at 85 °C. Of the silane coupling agents studied (see Fig. 4), we found that γ -aminopropyltriethoxy silane (A1100) significantly reduced the viscosity of bonded magnets at the very low silane concentrations used. The silane coupling agent, through a proposed chemical bonding model, forms a monolayer of an impervious coating or passivation layer, which has been identified as reducing significantly the thermal oxidation sensitivity of uncoated NdFeB powders, especially at high temperatures, as depicted in Fig. 4. Further, the chemical nature of the silane coupling agent selectively allows wetting of the coated magnetic NdFeB powders by the polymer and good adhesion between the coated magnetic powders and the polymer in the bonded magnet. Evidence confirming the homogeneous coating of the powders with the silane was obtained by SEM and Auger (data not shown for the purpose of brevity). The thermogravi-

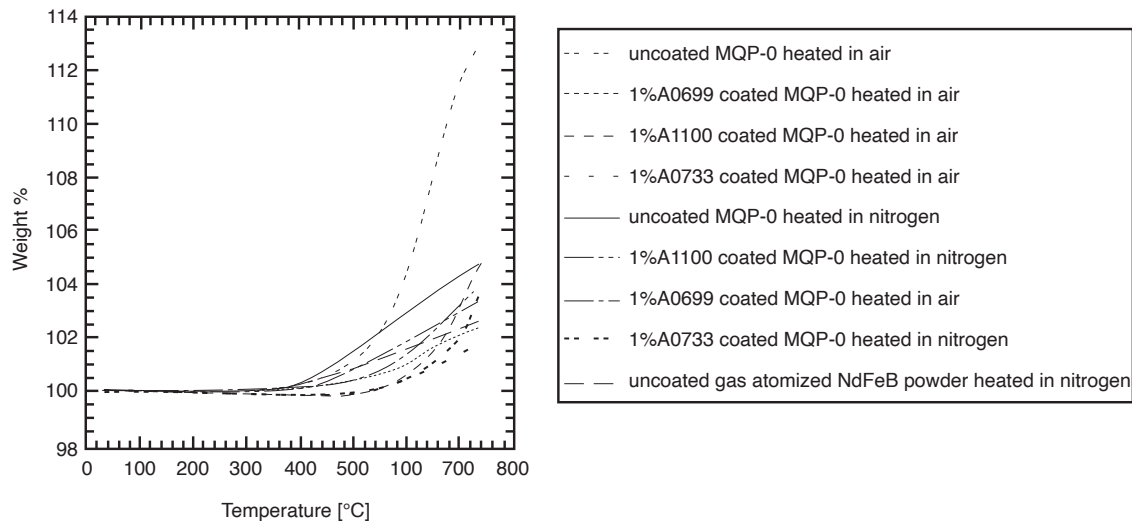


Figure 4 Effect of silane coupling agents on thermal oxidation of NdFeB powder. The coupling agents were A1100 ($C_9H_{23}NO_3Si$), A0733 ($C_{18}H_{41}NO_9Si$) and A0699 ($C_8H_{22}N_2O_2Si$).

metric analysis (TGA) results showed that the uncoated MQP-O powder was more stable than the uncoated gas-atomized powder, while silane modification of both powders increased their thermal oxidation stability.

To determine the thermal oxidation corrosion resistance of the silane coating, we measured the $(BH)_{max}$ of the PPS-bonded NdFeB magnets containing silane-coated and -uncoated NdFeB powders. The measurements showed that the $(BH)_{max}$ of samples containing gas-atomized powders as fillers were significantly lower than that of the bonded magnets containing MQP-O powder. Silane-modified NdFeB powders resulted in magnets having higher $(BH)_{max}$ than the magnets containing uncoated powders at an identical volume fraction of the powders (Table III). These results are consistent with the positive effect of silanes in improving the thermal oxidation resistance of the bonded magnets described earlier.

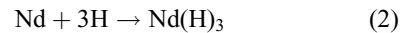
The observed thermal oxidation (or corrosion) of the uncoated NdFeB powders may be due to their direct oxidation in air, which is exacerbated in the presence of an aqueous electrolyte. In general, oxidation rates in air are low at temperatures below

150 °C, but very high corrosion rates can be produced in a humid environment. The rapid attack occurs via the preferential consumption of Nd- and B-rich phases on the grain boundaries, which causes the grains of the ferromagnetic phase to loosen causing the structural integrity of the magnet to be lost [8].

Under high temperatures and humid conditions, the corrosion mechanism of the NdFeB powders starts with a surface reaction of water vapor with the Nd-rich grain boundary phase according to the reaction:



The hydrogen produced above will then diffuse into the powder and react with the Nd-rich grain boundary phase, causing the observed corrosion:



The corrosion results in a volume expansion of the grain boundary phase, leading to decrepitation of the grain boundary. The hydrogen reaction with the Nd-rich grain boundary phase is the predominant mechanism in the humidity-related corrosion of NdFeB magnets. As mentioned earlier, corrosion of NdFeB in the PPS-bonded magnets is significantly reduced by the presence of the silane and polymer binder under normal-use temperatures of ≤ 180 °C. At temperatures in excess of the decomposition temperatures of the organic coating and the polymer, the corrosion mechanism of the pure NdFeB just described predominates.

In conclusion, it has been demonstrated that the processability, thermal corrosion resistance, and magnetic properties of PPS-bonded NdFeB magnets can be significantly enhanced by treating the NdFeB powders with a suitable silane coupling agent prior to blending with the polymer and subsequent molding of the composite. Further, detailed quantitative assessment of the effect of the corrosion behavior under extreme thermal and aggressive

TABLE III Relationship between the volume fraction of NdFeB filler and energy product of PPS-bonded NdFeB magnets

Sample No.	Volume Fraction, %	Energy product, MGOe
Filler: uncoated MQP-O		
1	38.7	1.985
2	38.9	2.08
3	39.1	2.12
Filler: coated MQP-O		
4	37.3	1.975
5	38.3	2.07
Filler: uncoated gas-atomized NdFeB powder		
6	37.8	0.629
7	35.7	0.547
Filler: coated gas-atomized NdFeB powder		
8	36.5	0.548
9	36.7	0.582

environments of the PPS-bonded NdFeB magnets can be obtained using standard long/short-term irreversible loss tests, which is the subject of a separate paper to be published elsewhere. Clearly, the surface treatments described in this letter may be easily adapted to other polymer-bonded magnets from which new magnetic devices with beneficial properties can be obtained.

Acknowledgments

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References

1. Z. OSAWA, K. KAWAUCHI, M. IWATA and H. HARADA, *J. Mater. Sci.* **23** (1988) 2637.
2. A. HANDSTEIN, K.-H. MULLER, R. GROSSINGER, H. R. KIRCHMAYR and R. KREWENKA, *J. of Magnetism and Magnetic Mater.* **101** (1991) 377.
3. M. HAMANO, *J. Alloys and Compounds* **222** (1995) 8.
4. T. ABRAHAM, *J. Metals* **47** (1995) 16.
5. V. PANACHANATHAN, *J. Mater. Engng and Perf.* **4** (1995) 423.
6. R. N. ROTHON, in "Surface modification and surface modifiers, particulate-filled polymer composites" edited by R. N. Rotheron (Longman Scientific & Technical, Essex, 1995) p. 137.
7. E. P. PLUEDDEMANN, in "Composite materials, Vol. 6," edited by E. P. Pluedemann (Academic Press, New York, 1974) Chapter 6.
8. A. S. KIM, F. E. CAMP and T. LIZZU, *J. Appl. Phys.* **79** (1996) 4840.

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