Enhancement of the Relative Magnetic Permeability of Polymeric Composites with Hybrid Particulate Fillers

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ABSTRACT: Composites with high relative magnetic permeability values can be used in many industrial applications, especially if they can be shaped using conventional polymer-processing technologies. In this study, various hybrid composite systems (i.e., particles with differing aspect ratio, size, and magnetic permeability embedded into a polymeric binder) were prepared in an attempt to reach high relative permeability values without the use of high pressures or sintering. It was determined that an interaction effect between the different types of fillers exists and enhances the relative magnetic permeability value of the composite in relation to the use of single type of magnetic filler. Relative magnetic permeability values of over 100 were achieved. Such relative magnetic permeability values represent a significant increase in the magnetic permeability over available magnetic composites prepared using similar processing techniques. The significant gains in magnetic permeability were realized by altering the maximum packing fraction, and ultimately the percolation threshold of the composite, by using low and high aspect ratio particles simultaneously in the formulation of the magnetic composites. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1371–1377, 1997

Key words: permeability; magnetic; composites; particulates

INTRODUCTION

Polymeric composites with magnetic properties can be prepared by combining a magnetic filler material with a polymeric host, i.e., a binder. This can be accomplished by using traditional polymer-processing techniques which afford several advantages over the traditional techniques for shaping ceramic and metallic magnets. Polymeric magnets of complex shapes can be manufactured with high production rates and low costs by utilizing polymer-processing operations including injection-molding. However, such technologies have been applied mainly to the fabrication of permanent magnets.[1–3] Nevertheless, since their first appearance in a French patent in 1955,[4] plastic magnets have found widespread use in many areas, including uses in electrical and electronic instruments, communication instruments, household utensils, and audio equipment.

Early researchers used soft ferromagnetic powder materials coated with an insulating polymeric binder to make dust cores. The insulating binder effectively increases the resistance of the core, thus reducing power losses. Here we probe and further elucidate the opportunities in tailoring the electrical and magnetic properties of composites by varying the amount and nature of the powder particles. This technique should allow the alteration of the permeability of the core over a wide range and lead to an increase in magnetic stability. Furthermore, by using multiple fillers the fi-

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Table I Relative Permeability of PE/Met/NiZn Composite Samples

Relative Permeability of PE/Met/NiZn			
	NiZn Ferrite (vol %)		
Metglas (vol %)	0	25	50
0	1.00	3.12	7.82
0	1.00	2.47	6.33
3	7.21	10.30	19.90
3	6.79	9.72	18.70
5	15.86	18.55	31.50
5	18.32	21.92	32.00
10	31.36	31.81	59.80
10	31.85	33.28	61.60
15	43.69	58.10	99.70
15	42.56	56.10	95.50

nal properties of the composite can be tailored to meet specific applications. For example, the maximum theoretical packing fraction of the composite can be altered by using particles with different shapes or size distribution.

High aspect ratio particles reduce the maximum theoretical packing fraction, i.e., the maximum amount of particulates which can be incorporated into a composite, while at the same time reducing the percolation threshold.[5] In addition, asymmetric particles can give rise to higher magnetization than symmetric particles.[6] Another possibility with multiple fillers is to combine particles with dissimilar properties. For example, the resistivity of the composite can be engineered by incorporating a magnetic ferrite with a metallic one.

Such multiple ferromagnetic particles, especially soft ones, can be incorporated into a polymeric binder, and the resulting composites become candidates for various industrial applications at low frequencies. For example, the stray magnetic fields produced by electrical instruments operating at low frequencies can present numerous problems. Shielding structures composed of composite materials with sufficiently high relative magnetic permeability could provide effective means in attenuating stray magnetic fields.[7]

BACKGROUND

It has been shown that at low loading levels the magnetic permeability of granular composites $\mu_r(\phi)$, increases linearly with the volume fraction, ϕ, of the filler[8]:

$$\mu_r(\phi) = 1 + A\phi \tag{1}$$

where A is a coefficient which depends on the magnetic properties of the filler, its shape, and its volume fraction. For example, for spherical particles the demagnetization factor is $N = 1/A = \frac{1}{3}$, so that eq. (1) becomes

$$\mu_r(\phi) = 1 + 3\phi \tag{2}$$

As the loading level, ϕ, is increased, the magnetic permeability value deviates significantly from this linear behavior and becomes a nonlinear function of the volume fraction.[8,9] Based on previous experimental studies,[8–10] the nonlinear dependence of the relative permeability on the volume fraction can be approximated by using a quadratic function:

$$\mu_r(\phi) = 1 + B\phi^2 \tag{3}$$

A hybrid magnetic composite may be defined as a composite containing two or more fillers with different magnetic properties, sizes, size distributions, and shapes. The relative permeability of a hybrid composite consisting of similar particles (size, size distributions, and shape) that differ only in magnetic properties may be expected to obey a simple quadratic additivity rule:

$$\mu_r(\phi_1, \phi_2) = 1 + B_1\phi_1^2 + B_2\phi_2^2 \tag{4}$$

Table II Relative Permeability of PE/Met/HyMu Composite Samples

Relative Permeability of PE/Met/HyMu		
	HyMu (vol %)	
Metglas (vol %)	0	50
0	1.00	8.36
0	1.00	9.36
3	7.21	54.30
3	6.79	45.10
5	15.86	60.70
5	18.32	57.80
10	31.36	91.60
10	31.85	101.60

Table III Summary of Analysis of Variance for PE/Met/NiZn Composite

Summary of All Effects for PE/Met/NiZn Composites						
Effect	df Effect	ms Effect	df Error	ms Error	*F*	*P* Level
1	2	1520.1	15	1.842	825	0.000000
2	4	3723.7	15	1.842	2020.9	0.000000
12	8	208.1	15	1.842	113	0.000000

It may be possible to achieve higher magnetic permeability values for hybrid composites by using dissimilar shapes and sizes of filler particles. For instance, Hashin and Shtrikman[11] give bounds of the magnetic permeability for a densely packed composite consisting of coated spheres. By using a variational approach they were able to determine the bounds to be

$$\mu_1 + \frac{3\phi_2\mu_1(\mu_2 - \mu_1)}{3\mu_1 + \phi_1(\mu_2 - \mu_1)} \le \mu_e \le \mu_2 + \frac{3\phi_1\mu_2(\mu_1 - \mu_2)}{3\mu_2 + \phi_2(\mu_1 - \mu_2)} \quad (5)$$

provided $\mu_2 \ge \mu_1$. The lower bound of the inequality corresponds to the situation where component 2 with a relative permeability of μ_2 is coated with component 1 with a relative magnetic permeability of μ_1. The upper bound corresponds to a composite where component 1 is coated with component 2. By tailoring a composite with flexible flakes and spherical particles, it may be possible to achieve the upper bound of the effective magnetic permeability. If the flexible flakes are large in comparison to the spherical particles and have a greater magnetic permeability, then the flakes can act as if they are "coating" the spherical particles, resulting in an enhanced magnetic permeability value.

The objective of this study was to determine whether the permeability of a magnetic composite would be enhanced with the incorporation of hybrid fillers. In addition, the functional dependence of the volume fractions of each filler was studied to determine their effects on the magnetic permeability of the composites.

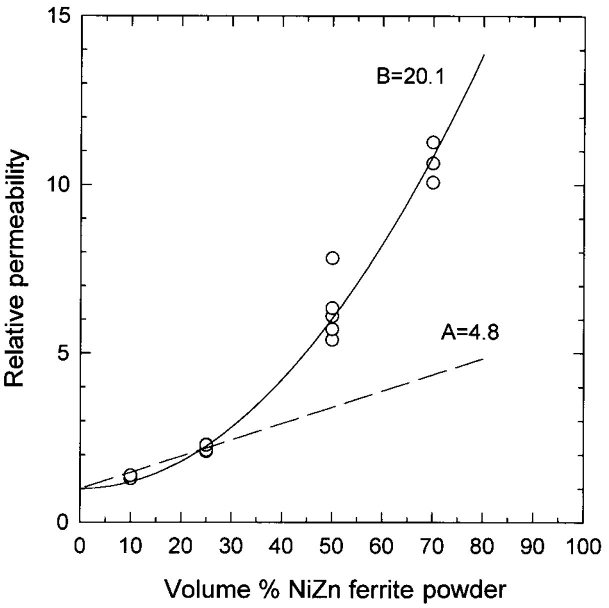

Figure 1 Relative permeability of NiZn composites as a function of filler concentration.

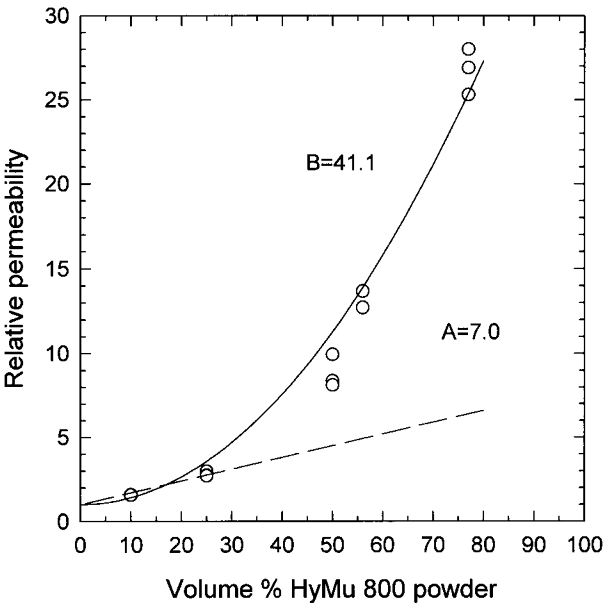

Figure 2 Relative permeability of HyMu composites as a function of HyMu concentration.

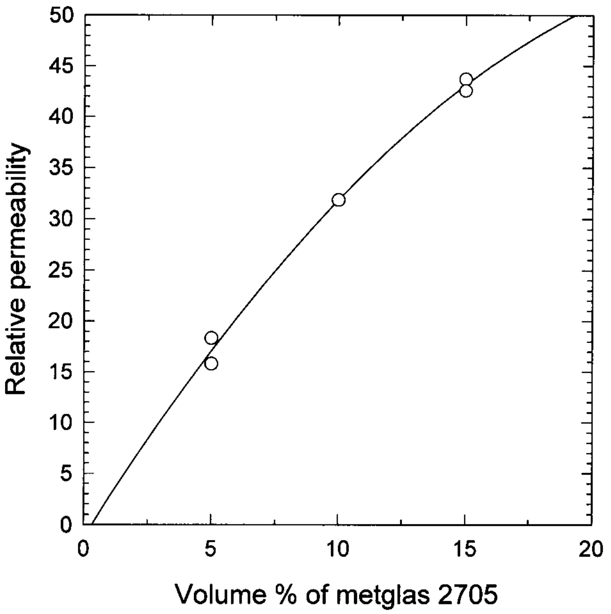

Figure 3 Relative permeability of Metglas 2705M composites as a function of Metglas concentration.

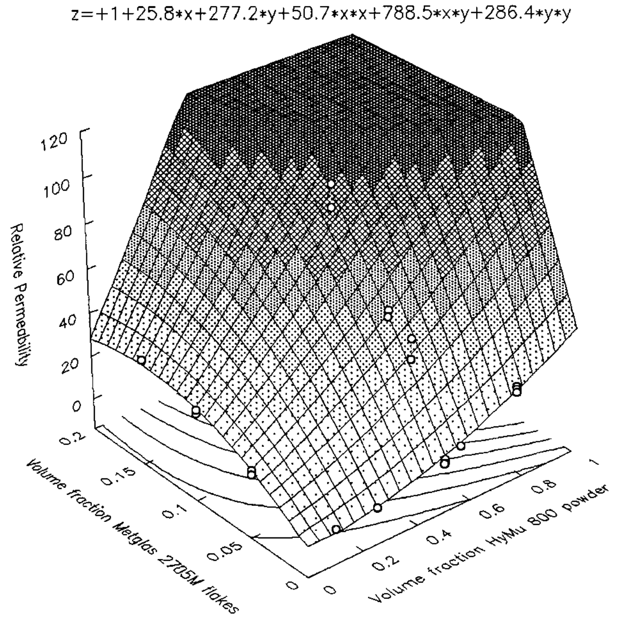

Figure 5 Relative permeability of the hybrid HyMu 800/Metglas 2705M composites.

EXPERIMENTAL

Materials

Three magnetic materials were chosen for this study: a ferrite powder, an amorphous metal ribbon cut into flakes, and a ferromagnetic metal powder. The ferrite powder, code 28, was supplied by D. M. Steward MFG Co. (Chattanooga, TN). The 28 material is a fully reacted nickel–zinc spinel ferrite with an average particle diameter of 60 μm. The particle size distribution was narrow and the particles ranged in size from 50 to 70 μm. The amorphous ribbon, trade name Metglas "Met" 2705M, was obtained from Allied Signal (Morristown, NJ). It has a chemical composition of 69% cobalt, 12% boron, 12% silicon, 4% nickel, and 2% molybdenum. The Metglas was supplied as a continuous ribbon of 1-in. width and 0.8-mil thickness. The ribbon was cut into flakes with an aspect ratio of 1,250 (ratio of largest dimension to thickness). The metallic ferromagnetic filler was HyMu 800, procured from Carpenter Technology Corp. (Reading, PA). HyMu 800 has a composition of 80% nickel, 5% molybdenum, 0.5% manganese, 0.15% silicon, 0.10% carbon, and the balance iron. It was supplied in spherical powder form at −100 mesh. The polymer matrix used in this study was low-density polyethylene (LDPE), Petrothene PEV 007, available from USI Chemicals (Cincinnati, OH).

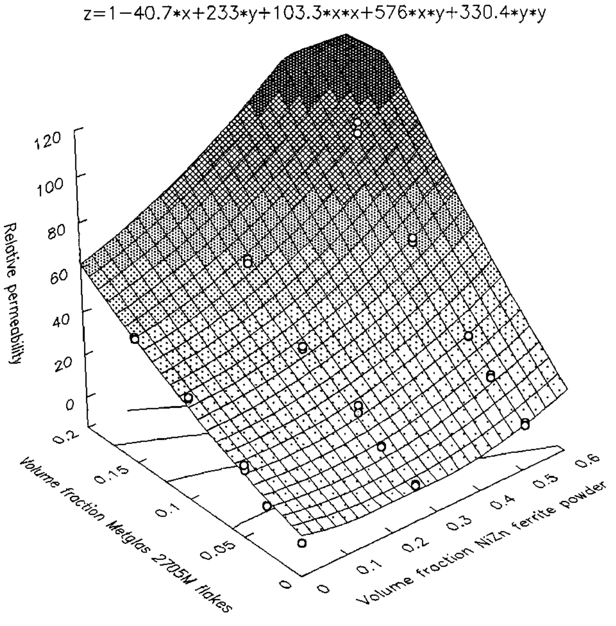

Figure 4 Relative permeability of the hybrid NiZn/Metglas 2705M composites.

The experimental setup and material preparation techniques for mixing, determination of particle attrition, molding of ASTM specimens, and characterization of magnetic permeability values which we used here were the same as those reported earlier.[12]

Table IV Significance of Estimated Parameters in Eq. (6) for the PE/Met/NiZn Composite System

	Parameter in Eq. (6)				
	B1	B2	B3	B4	B5
Estimate	−40.7	103.3	233	330.4	575.9
Standard error	10.9	22.7	22.8	144.5	52.9
t	−3.72	4.56	10.2	2.3	10.9
p-level	0.001	0.0001	0.0000	0.0309	0.0000

RESULTS AND DISCUSSION

For the evaluation of hybrid composites, two composites systems were used. One was a combination of PE/Met/NiZn ferrite and the other was a mixture of PE/Met/HyMu. Both were prepared at various loading levels. The PE/Met/NiZn system study was conducted as a two-factor design experiment with five levels of the Metglas 2705M concentration and three levels of the NiZn concentration. The PE/Met/HyMu system was run at four levels of the Metglas 2705M concentration and two levels of the HyMu concentration. Tables I and II show the experimental design and summarize the results for both systems.

The results of an analysis of variance on the PE/Met/NiZn composite system showed that the interaction between the two fillers was very significant, as seen in Table III. Orthogonal contrasts and Tukey's test were used to demonstrate that the main effects were significant at all levels. An analysis of variance, orthogonal contrasts, and Tukey's test conducted on the PE/Met/HyMu composite system revealed that the main effects and interactions were also significant for this system. The small incremental change in Metglas concentration from 3% to 5% was only marginally significant.

The data in Tables I and II are depicted graphically in Figures 1–5. Figures 1–3 show the results of magnetic relative permeability of single-filler composite systems. The dashed lines in Figures 1 and 2 represent a curve fit to the data at low loading levels, i.e., 10% and 25% loading levels, to eq. (1). The solid lines in Figures 1–3 represent the regression analysis, best fit to eq. (3), of the data for the entire range of volume loading levels. The most striking feature about Figures 1 and 2 is the relative permeability increase at high loading levels, as indicated by the difference between the solid and dashed lines. Also note the difference between the two types of fillers. The NiZn filler produces coefficients of $A = 4.8$ and $B = 20.1$, while the HyMu filler has coefficients of $A = 7.0$ and $B = 41.1$. The differences in coefficients are due to the differences in intrinsic magnetic qual-

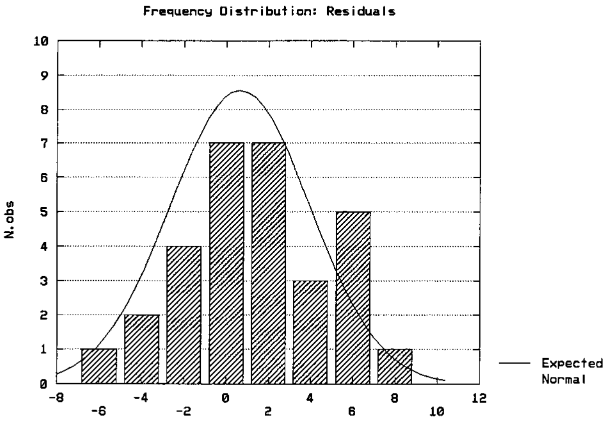

Figure 6 Distribution of residuals for regression of eq. (6) to PE/Metglas/NiZn data.

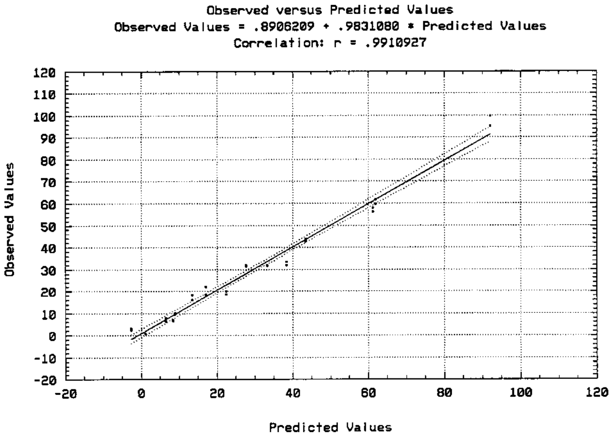

Figure 7 Predicted values from eq. (6) versus observed values for PE/Metglas/NiZn composites.

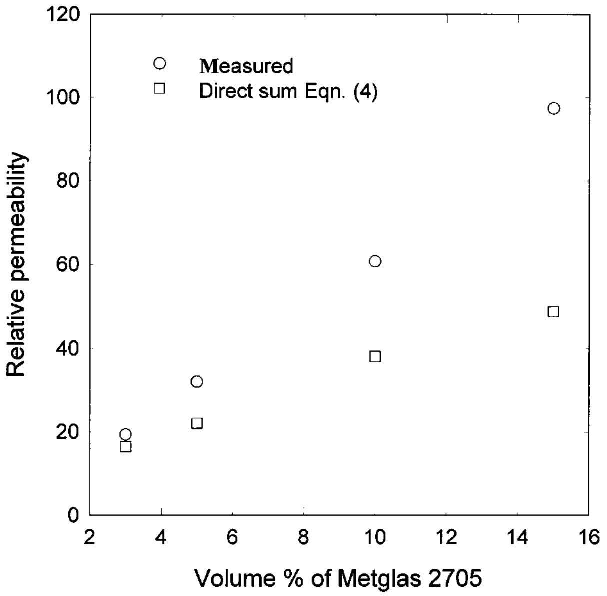

Figure 8 Relative permeability of PE/Metglas/NiZn composites with 50% NiZn and as a function of volume percent of Metglas.

ity, size, shape, and size distributions between the two filler particles.[9]

The relative permeability values of composites containing Metglas flakes exhibit a different trend than those with the powders, as indicated in Figure 3. The relative permeability values of the composite increase with increasing volume loading level of the Metglas. However, the rate of change of the permeability with increasing concentration decreases here, as opposed to the powder samples, which increase with an increasing rate (Figs. 1 and 2). This may be due to the fact that at high loading levels the mixing process produces high stresses which can degrade the intrinsic permeability as well as the aspect ratio of the flakes.

Figures 4 and 5 are the three-dimensional surface plots of the two composite systems with the hybrid fillers. Figure 4 shows the relative permeability of the PE/Met/NiZn composite system as a function of the volume fractions of Metglas and NiZn. The regression equation for this surface is

$$\mu_r = 1 - 40.7\phi_1 + 233\phi_2 + 103.3\phi_1^2 + 576\phi_1\phi_2 + 330.4\phi_2^2 \quad (6)$$

where ϕ_1 is the volume fraction of the NiZn filler and ϕ_2 is the volume fraction of the Metglas. It is evident from Figure 4 that there is a significant interaction between the two fillers which enhances the overall relative permeability of the composite system. This enhancement manifests itself by the modification of the second-to-last term in eq. (6), i.e., $576\phi_1\phi_2$, which is an indication of the strength of the interaction between the two fillers. This term is not accounted for in eq. (4). Table IV summarizes the significance of the estimated parameters to eq. (6). The correlation coefficient for eq. (6) is 0.9911. The regression model accounts for over 98.2% of the variation in the data. A plot of the distribution of residuals reveals a normal behavior as shown in Figure 6. Figure 7 is a plot of the best fit versus the experimental values. Figures 6–8, combined with the correlation coefficient and the p-level of the parameters, indicate that the proposed model of eq. (6) is indeed a valid one.

The relative permeability values of the PE/Met/HyMu composite samples are shown in Figure 5. Again the enhancement is apparent with the use of hybrid fillers. The regression equation for this surface is

$$\mu_r = 1 + 25.8\phi_1 + 277.2\phi_2 + 50.7\phi_1^2 + 788.5\phi_1\phi_2 + 286.4\phi_2^2 \quad (7)$$

where ϕ_1 is the volume fraction of the HyMu filler and ϕ_2 is the volume fraction of the Metglas. Again there is a large interaction term between

Table V Relative Magnetic Permeability of PE/Metglas/NiZn Composite

PE/Met/NiZn (vol %)	Relative Permeability	Average	Direct Sum	Enhancement (%)
47/3/50	19.9, 18.7	19.3	16.4	18
45/5/50	31.5, 32.0	32.0	22.0	46
40/10/50	59.8, 61.6	60.7	38	60
35/15/50	99.7, 95.0	97.4	48.7	100

Table VI Relative Magnetic Permeability of PE/Metglas/HyMu Composite

PE/Met/HyMu (vol %)	Relative Permeability	Average	Direct Sum	Enhancement (%)
47/3/50	54.3, 45.1	49.7	18.6	168
45/5/50	60.7, 57.8	59.3	26.1	127
40/10/50	91.6, 101.6	96.6	42.4	128

the fillers, $788\phi_1\phi_2$, which enhances the permeability.

Another way to illustrate the enhancement of relative permeability values with hybrid fillers is to compare the actual values with those predicted by eq. (4), i.e., the direct sum of the single-filler composite systems that compose the hybrid system. These values are compiled in Tables V and VI. An examination of the tables shows that the measured values are always greater than those predicted by the simple quadratic additivity rule (denoted as "direct sum") provided by eq. (4). This is emphasized in Figure 7, where the permeability values of hybrid composite samples containing 50% NiZn ferrite and varying amounts of Metglas are plotted. Also plotted are the direct sums of the single-filler composite systems which make up the hybrid system. Again these results show that the enhancement of the relative permeability of hybrid composites is greater than can be accomplished by using high loading levels of the individual fillers.

The hybrid systems used here, we believe, generate the highest relative permeability values for this class of materials, i.e., soft ferromagnetic composites with high binder content (greater than a few percent). The high binder content allows for flow-based processing operations and the final composites do not require sintering. This technique is amenable to three-dimensional structures where injection-molding operations are advantageous. To our knowledge this method has not been previously exploited.

CONCLUSIONS

Two hybrid composite systems were prepared at various filler concentrations and were characterized in terms of their relative magnetic permeability values. It was shown that the use of hybrid composites with symmetric and asymmetric particulates produces a synergistic enhancement of the relative magnetic permeability values when compared with the magnetic permeability values of the individual filler systems which comprise the hybrid system. This type of synergism has hitherto not been reported in the literature, and generates relative permeability values which are greater than any that have been reported in the literature.

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