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Optimization of magnetic and dielectric properties of surface-treated magnetite-filled epoxy composites by factorial design

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ABSTRACT

The effect of surface modification parameters such as 3-aminopropyl triethoxysilane (3APTES) coupling agent concentration (5, 10, and 20 wt%) and treatment duration (3, 5, and 7 h) were studied using design of experiment (DOE) approach. A quadratic model was developed based on response surface analysis. Analysis of variance (ANOVA), R-squared (R-Sq), and normal plot of residuals were applied to determine the accuracy of the models. Multiple responses were simultaneously analyzed by optimization. Magnetic and dielectric properties were used as composite system responses. Solution 1 with 16.66 wt% silane and 7 h treatment time was selected for optimum response. Confirmation study showed that predicted response values match the experimental results.

1. Introduction

Ferrite polymer-based composites with high permeability, high dielectric constant, and low dielectric loss are gaining attention in various areas such as embedded passive magnetic component, coils, and on-chip electromagnetic shielding applications. The dielectric and magnetic behavior of these ferrite-based polymer composites must be properly understood [1–3]. During ferrite polymer preparation, ferrite particles tend to agglomerate because of strong magnetic particle interactions [4–6]. Inhomogeneous ferrite in the polymer generally leads to the formation of defects in the composite, which affects the quality and performance of the magnetic devices. Surface treatment of ferrite fillers with a coupling agent in the polymer matrix improves matrix filler dispersion and enhances the compatibility of the ferrite fillers and matrix.

A number of parameters during the surface functionalization affect the surface treatment, including coupling agent type and concentration as well as treatment time [7]. All these parameters have not been studied simultaneously and are assumed to have no effect on one another [8–10]. These experiments are considered as single factor experimentation and are referred to as one-factor-at-a-time or OFAT. OFAT is a method of designing experiments where each factor is tested sequentially with all other factors held constant [11]. However, OFAT was found to be inefficient and inadequate in providing valid information. The information obtained often does not justify the resources expended [8].

Design of experiment (DOE), also known as experimental design, is a method commonly used to statistically evaluate the effect of one or more variables on an output through experimental runs [12]. DOE has been applied extensively, especially in the field of science and engineering [13,14]. DOE enables scientists to optimize and predict the possible output based on parameter settings. DOE is an experiment-based modeling whereby a systematic approach is used during experimental planning, data collection, and data analysis. Thus, DOE is far superior to the OFAT approach. DOE is used mainly because it shows the relationship between parameters and responses, providing significant information and better explanation than the OFAT method. In addition, DOE saves time and cost because the number of runs is determined before the actual experiment [15].

In the present study, DOE was utilized to optimize the surface modification condition of magnetite-filled epoxy thin film composite properties. Analysis of variance (ANOVA), R-squared (R-Sq), and normal plot of residuals were applied to determine the accuracy of the models. Optimization was used for simultaneous multiple response analysis. The responses used were the magnetic and dielectric properties of magnetite-filled epoxy thin film composites.

2. Experimental

2.1. Materials

Magnetite (Fe_3O_4) was purchased from Sigma-Aldrich. Magnetite has a density of 4.95 g/ml, a particle size of less than 100 nm, and a molecular weight of 231.53 g/mol. Epoxy resin based on bispenol-A-epichlorohydrin (DER™ 332) was used as a resin with

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an epoxide equivalent weight of 182 g/eq. to 192 g/eq. and a density of 1.66 g/ml. Polyetheramine PEA (D230) with a density of 0.946 g/ml was used as a curing agent.

2.2. Surface modification of magnetite filler

In this study, magnetite fillers were treated with silane coupling agent at different concentrations (5, 10, and 20 wt%) and treatment time (3, 5, and 7 h). Magnetite fillers were added in an ethanol solution and ultrasonicated for 10 min for dispersion. Ethanol solution was prepared by diluting ethanol with deionized water with a ratio of 95:5. Then, a weighed amount of silane was added into the suspension. Formic acid was added into the mixture until pH 4 was achieved. The mixture was then stirred for 10 min to obtain homogeneity. Subsequently, the mixture was continuously stirred at 60 °C for 3, 5 and 7 h treatment time. Then, the silane-treated magnetite was washed with water followed by ethanol. The modified magnetite was then dried in an oven at 60 °C for 12 h.

2.3. Preparation of treated magnetite-filled epoxy polymer composites

Approximately 20 ml chloroform, as dispersion medium, was added to the weighed particles. The mixture was stirred in an ice-water bath for 10 min using an ultrasonic stirrer (UP 200S, Hielscher) to break up large aggregates. Next, DER™ 332 was added to the suspension at a specific weight percentage basis and ultrasonically stirred for 15 min. The solution was placed and dried in a vacuum oven at 45 °C for 30 min to remove the excess chloroform. Then, curing agent PEA (D230) with a resin-to-hardener ratio of 100:32 was added to the mixture and mixed quickly for 3 min to ensure even filler distribution. To remove bubbles, the mixture was subjected to vacuum for 15 min at room temperature. The mixture was then deposited onto a transparency and spin coated at 250 rpm for 30 s, followed by 500 rpm for 30 s and 750 rpm for 60 s. The composite films were then cured at 80 °C for 2 h.

2.4. Characterization

A vibrating sample magnetometer was used to evaluate the room temperature magnetic parameter of the polymer composites with an applied field range of –20 kOe to 20 kOe. Dielectric properties of the polymer composites were measured over the range of 10^6 Hz to 10^9 Hz using Hewlett Packard 4291B impedance analyzer. Factorial designs of 3^2 were constructed with two factors and three levels. The identified factors were silane amount and treatment time. The factor levels are shown in Table 1. The full factorial design with single replicate involved nine random runs. For the experimental analysis, the design matrix was created by using Design Expert 6.0.6 as shown in Table 1.

Table 1
Factors and levels of experiments.

Levels	Low	Medium	High
Factors	(−1)	0	(+)
Amount of silane (%)	5	10	20
Treatment duration (h)	3	5	7

3. Results and discussions

The objective of DOE is to determine the optimal values of the two numerical factors, silane amount and treatment duration, and optimize the actual response. The actual optimized responses are saturation magnetization, dielectric constant, and dielectric loss. The experimental results are summarized in Table 2, and these data were used as input into the DOE software for analysis.

3.1. Analysis and model fitting for the responses

Multiple regression analysis was applied to develop the mathematical model or statistical equation for the desired response as a function of variable. Data obtained from the experimental technique were fitted into the mathematical model (Eq. (1)):

$$Y=\beta_0+\sum_{i=1}^{k}\beta_i X_i+\sum_{i=1}^{k}\beta_{ii}x_i^2+\sum_{i<j}\beta_{ij}x_i x_j+\varepsilon \tag{1}$$

where Y is the response (dependent variable), and x_i and x_j are the factors (independent variables). β_0 is the model constant, β_i is the linear coefficient, β_{ii} is the quadratic coefficient, β_{ij} is the interaction coefficient between x_i and x_j, and ε is the standard error.

To understand the impact of various control factors on the response of experimental data, ANOVA was used to determine the significant factors. Meanwhile, the adequacy of the developed models can be verified through regression analysis and normality.

3.1.1. ANOVA

The purpose of ANOVA is to determine the factors and their interactions that significantly affect the process. Tables 3–5 summarize the results of ANOVA for saturation magnetization, dielectric constant, and dielectric loss, respectively. The “Model *F*-value” of 22.44 for saturation magnetization, as shown in Table 3, shows that the model is significant and only a 0.04% chance exists that a “Model *F*-value” this large could occur due to noise. *P* value represents the significance level, whether suitable or unsuitable. Values of “Prob > *F*” less than 0.05 indicates that the model is significant. Such a condition is desirable, indicating that the terms in the model has significant effect on the response (saturation magnetization).

Table 2
Experimental design and actual responses of saturation magnetization, dielectric constant, and dielectric loss.

Run no.	Variables		Actual responses		
	Silane amount (wt%)	Treatment duration (h)	Saturation magnetization (emu/g)	Dielectric constant (at 1 GHz)	Dielectric loss (at 1 GHz)
1	10	5	15.81	2.07	0.033
2	20	7	17.46	2.42	0.042
3	20	5	14.72	2.15	0.035
4	20	3	14.21	1.91	0.028
5	10	3	14.25	1.89	0.027
6	10	7	17.80	2.38	0.040
7	5	7	15.98	2.26	0.038
8	5	3	14.21	1.88	0.026
9	5	5	14.59	2.00	0.032