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DEVELOPMENT AND CHARACTERIZATION OF THE THERMAL EXPANSION OF FIELD STRUCTURED MAGNETIC COMPOSITES

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ABSTRACT

Polymer composites containing magnetic fillers are promising materials for a variety of applications, such as in energy storage and medical fields. To facilitate the engineering design of respective components, a comprehensive understanding of the thermomechanical behavior of such inhomogeneous and potentially highly anisotropic materials is important. The focus of the work presented herein is on the coefficient of thermal expansion (CTE) of the composites. The authors created field structured magnetic composites employing a permanent magnet-based particle alignment system. An epoxy polymer matrix was modified with a commercial-grade thickening agent. Anisotropic magnetic particles were added as the functional filler. The microstructure morphology, especially the filler distribution, dispersion, and alignment, was characterized using microscopy techniques. The CTEs of the composites were experimentally characterized in three directions, i.e., parallel, 45°, and perpendicular to the magnetic field direction. The setup designed for the CTE characterization features a hot-plate and an optical extensometer. The crystal structure of the composites, related to the magnetic filler material, was characterized by X-ray diffraction. This research demonstrates a method for CTE characterizing, and thus contributes to the creation, of designed structured magnetic composites.

1 INTRODUCTION

Reinforced polymer composites (RPCs), especially those with thermoset polymer based matrices like epoxy, have widely been applied in fields like aerospace and medicine, which is motivated by their attractive properties, including low density and good mechanical properties [1]. The coefficient of thermal expansion (CTE) is an important aspect to consider for RPCs due to the CTE mismatch between the reinforcement phase and the matrix. This mismatch plays an important role for the development of internal stresses during fabrication and latter utilization at different temperatures [2-3]. As a result, matrix cracking and debonding between the matrix and reinforcement material may occur. Also, since polymers typically have a high CTE, adding fillers is a means for reducing the CTE of the resulting composites, which is common for electrical devices [4-6]. Based on these considerations, it is important to acquire detailed knowledge of the thermal expansion effects of such materials. Pinheiro and Rosenberg [2] studied the influence of fillers with different sizes reinforcing an epoxy, i.e., copper and glass, on the thermal expansion characteristics. They found that below the polymer glass transition temperature (T_g) the CTE was independent of particle size, while above T_g, smaller particles yielded reduced thermal expansion. Tognana et al. [3] studied the influence of aluminum powder (up to 25 vol.%) on thermal expansion in composites with both the polymer matrix being in a glassy and rubbery state. Shi et al. [4] studied the influence of graphene microstructural features on the CTE in epoxy composites using an effective medium approach using Green's function method. Lin et al. [5] fabricated $GaNMn_3$ powders to reinforce epoxy composites with different filler loading, leading to improved and tunable heat conductivity, hardness, dielectric properties and CTE for electrical devices. Shirasu et al. [6] prepared aligned multi-walled carbon nanotube reinforced epoxy composites. Interestingly, they reported a CTE of zero over a temperature range from -5°C to 85°C at certain filler contents.

Neodymium iron boron (NdFeB) has been a promising filler with wide application in energy storage, mobile electronics, and aerospace. The CTE of NdFeB reinforced epoxy polymer composites is an important aspect in these applications, especially for anisotropic NdFeB powders which have different CTEs parallel and perpendicular to the orientation of the plate-like fillers, i.e., 4 to 9×10^{-6} K^{-1} and -2 to 0×10^{-6} K^{-1}, respectively [7]. Notably, alignment of anisotropic NdFeB composites can be achieved by applying an external magnetic field, imparting composite anisotropy. Consequently, in the present study, an epoxy polymer was modified with anisotropic NdFeB particles and a thickening agent to control particle settling during fabrication. A uniaxial magnetic field was used to structure the composites during curing. Samples were tested for their CTE by measuring the elongation with temperature in different filler alignment directions. The T_g of samples was measured, and X-ray diffraction (XRD) was employed to observe the orientation/anisotropy of fabricated magnetic composites.

2 Materials and Methods

2.1 Materials

Anisotropic NdFeB magnetic particles (type MQA-36-18, Magnequench, Pendleton, IN, USA) were used as the filler phase. An EPON 826/EPICURE W (Miller-Stephenson, Danbury, CT, USA) resin system modified with 2wt% of AEROSIL R202 (Evonik, Parsippany, NJ, USA) was used to embed the fillers. The particle loading of the epoxy composites was designed to be 12:88, named herein P-12vol%. The base resin, EPON 826, is a diglycidyl ether of bisphenol-A epoxy resin with an epoxide equivalent weight of 178-186. EPIKURE W is methylene dianiline curative with nitrogen content between 15.7% and 15.9%. The epoxy resin and hardener were mixed at a ratio of 100:26.4 by weight. The AEROSIL R202 modifier, a fumed silica surface treated with polydimethysiloxane, was added as an anti-settling agent for the magnetic particles by increasing the viscosity of the polymer. The material density and mass fraction for the various constituent materials for the P-12vol% samples are listed in Table 1.

Table 1. Constituent material density and mass fraction for the magnetic composite.

Material	MQA-36-18	EPON 826	EPICURE W	AEROSIL R202
Density (g/cm^3)	7.51	1.16	1.20	0.60
Mass fraction (%)	47.17	40.96	10.81	1.06

2.2 Materials Fabrication and Characterization

Material portions were weighed to a precision of 1 mg with the batch mass of 100 g. Epoxy resin and hardener were mixed by a SpeedMixer (FlackTek SpeedMixer, Landrum, SC, USA), followed by adding the AEROSIL R202 additive. Then, the magnetic particles were incorporated into the liquid phase. Mixing at each step occurred at a speed of 1200 rounds per minute for 2 min. The mixture was transferred into a aluminum mold with a round cavity with diameter of 127 mm. The mold with mixture was placed into a magnetic alignment jig, see Fig.1(a), which were then placed inside an oven (Isotemp Oven, Fisher Scientific, Ottawa, ON, Canada) applying heat at 75°C for 27 h until the mixture was cured forming a solid circular disk. Afterwards, the material was allowed to cool to room temperature inside the oven. Fabricated samples were subjected to post-curing in the oven for 24 h at 75°C.

As shown in Fig.1(a), the uniaxial magnetic field jig features a Halbach array containing 24 cylindrical permanent magnets (type NdFeB-N42 with diametral magnetization, K&J Magnetics, Pipersville, PA, USA), which are held inside a PTFE ring and encompassing aluminum tray. To design the mold and determine the magnetic field strength, finite element method magnetics (FEMM) developed by QinetiQ North America was employed (Waltham, MA, USA). The simulated uniaxial and uniform magnetic field strength was 0.3 T as shown in Fig.1(b).

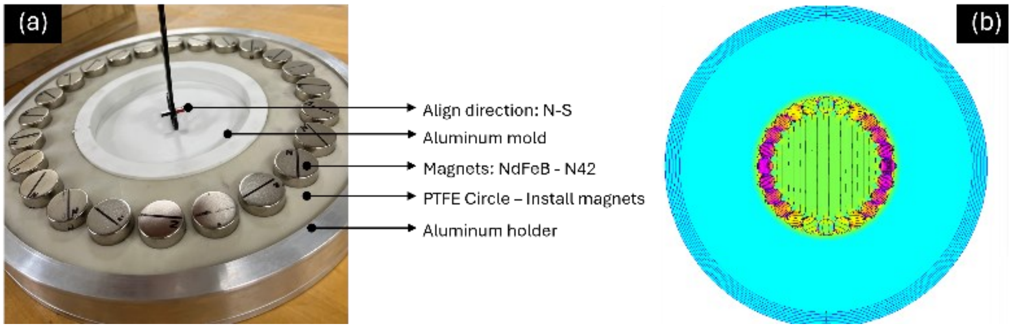

Figure 1. Mold for magnetic filler alignment: (a) Halbach array of 24 permanent magnets, and (b) magnetic FEM analysis used to simulate magnetic field direction and strength.

The T_g of fabricated P-12vol% samples was characterized by differential scanning calorimetry (DSC, DSC Model 1, Mettler Toledo, Columbus, OH, USA). Crushed powder with a mass of around 5 mg was placed into aluminum pans with lids. An iso-temperature test was first conducted at 25°C for 5 min. Then, the temperature was ramped to 300°*C* at 5°C/min. Tests were conducted under a nitrogen flow of 50 mL/min to maintain stable and consistent conditions. The STARe Excellence Thermal Analysis Software was used to determine the T_g of the samples.

CTE data for the P-12vol% samples were measured using the experimental setup schematically shown in Fig.2. Samples were tested in the direction parallel (0°), 45°, and perpendicular (90°) to the filler alignment direction. The dimensions of the specimens were 10 mm × 5 mm × (3 to 5) mm (length × width × thickness). The specimens were placed inside the cavity of an aluminum plate (cavity dimensions: diameter 20.5 mm, thickness 10 mm). The aluminum plate was placed on top of a hot plate (model S46415 Cimarec 1, Barnstead/Thermolyne, Dubuque, IA, USA). A fan was placed next to this setup for the cooling stage. Temperatures were measured by three mounted thermocouples placed on the top and side surfaces of the aluminum plate and on top of a dummy sample included in the setup. The specimen length change was measured by a laser device (type ONE-78PT-200, Epsilon Technology, Jackson, WY, USA) during heating and cooling. Two white lines were marked using a paint pen on the top of the specimen, close to the specimen extremities. These lines served as an optical extensometer to track length changes over a temperature range of 30 to 150°C. Three heating and cooling cycles were performed. Temperature and extensometer data were collected by a 4-Channel C Series Universal Analog Input Module along with a laptop computer using the NI-DAQExpress software (National Instruments, Austin, TX, USA).

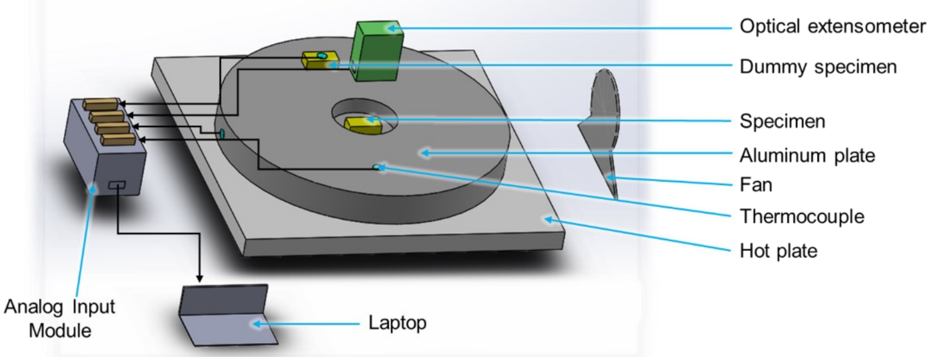

Figure 2. Schematic illustration of the experimental setup for determining CTE of matrix and P-12vol% samples.

Reduction of the collected data according to Eq.(1) yielded the CTE results for a given specimen.

$$\alpha = \frac{\Delta L}{\Delta T} \times \frac{1}{L_0} \quad (1)(3)(2)(1)$$

where α is the sample CTE, ΔL is elongation with temperature, ΔT, L_0 is the initial gauge length between the marker lines. The slope of the elongation to temperature curve was computed using the “linear best fit” feature in the OriginPro software (OriginLab, Northampton, MA, USA), with α being the quotient of slope and L_0.

XRD analysis was utilized to characterize the crystal structures of the P-12vol% samples in three different directions, i.e., 0°, 45° and 90° (type D8 Discover Plus, Bruker, Billerica, MA, USA). The EIGER2R_500K detector with 2D mode and “snapshot” was chosen for this characterization, i.e., 2θ = 44°, 1 step and scanned for 1800 s.

3 Results and Discussion

From the DSC study, the T_g was measured as 92.6°C. Based on this value, a temperature of 95°C was set as a threshold to calculate the linear portion of the CTE, assuming that chain mobility of the polymer phase changes above T_g, causing a non-linear behavior. As an example, Fig.3(a) depicts the sample elongation in filler alignment direction when temperature was increase from 40 to 140 °C for three heating cycles. It is apparent that the signals are rather noisy for the heating process, which presumably is caused by hot air distortion affecting the optical extensometer. Also, the elongation data for the first heating cycle deviates noticeably from the second and third cycle. It is postulated that a post-curing effect took place leading to an increased degree of cure of samples with subsequent heating cycles [2-3]. Given that data from the second and third cycles are nearly congruent, the CTE was analyzed from these two cycles. Figure 3(b) shows data for both heating and cooling for the second and third cycle (again for the filler alignment direction). It can be observed that data collected during cooling was considerably less noisy than for the heating stage. Thus, CTE data were computed solely based on the elongation measured during cooling. Notably, linear behavior and close congruence between the curves could only be ascertained below approximately 95°C, which is consistent with the measured T_g. Consequently, CTE data was distinguished for two temperature ranges, i.e., 40-95°C and 95-140°C.

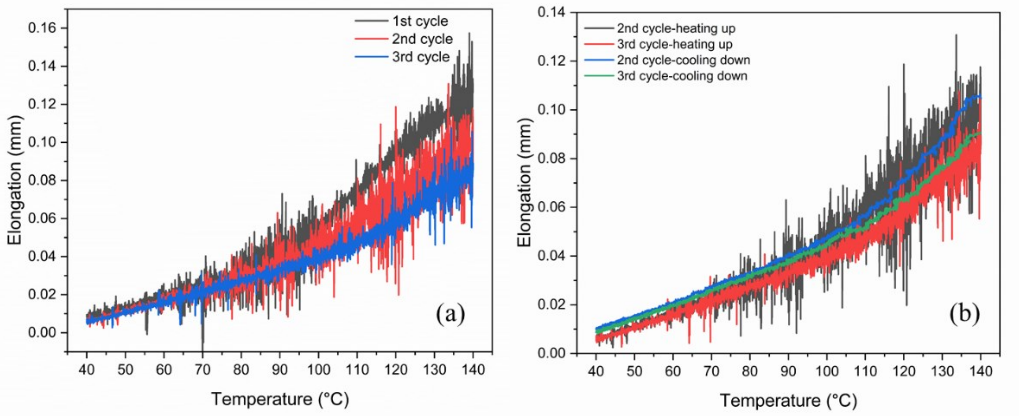

Figure 3. Sample elongation measured from 40 to 140°C: (a) heating cycles, and (b) second and third heating/cooling cycles.

Illustrated in Fig.4(a) and (b) are the elongation versus temperature curves from the second and third cooling cycles for three specimen orientations (0°, 45° and 90° with respect to the filler alignment), respectively. An increase in slope can be observed when transitioning from the 40 to 95°C to the 95 to 140°C temperature range. It can also be seen that in each of the temperature ranges the slopes are not parallel for the different specimen orientations, which indicates that CTEs vary with the filler alignment direction.

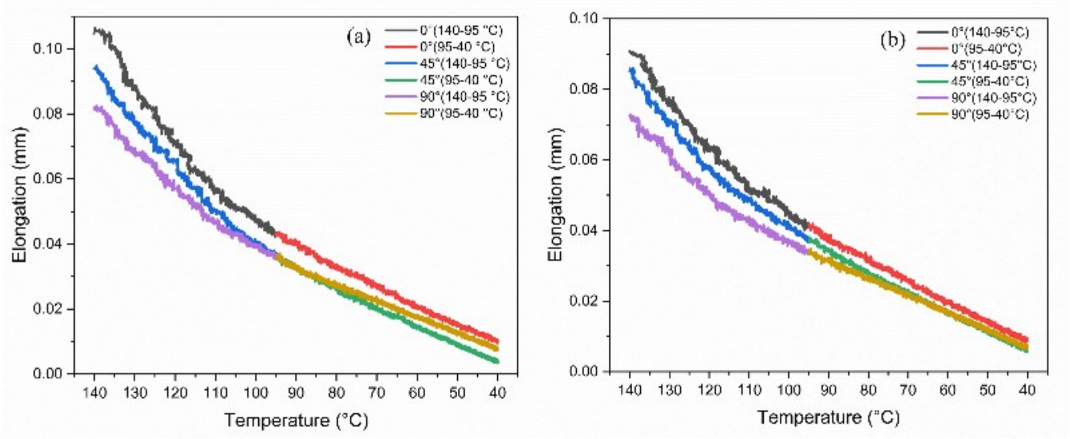

Figure 4. Elongation versus temperature for different specimen orientations: (a) second and (b) third cooling cycles.

The calculated CTEs along with the coefficient of determination (R^2) for the two different temperature ranges are listed in Table 2. The results show a decrease in CTE with increasing deviation from the filler alignment direction. R^2 values for the 40 to 95°C temperature range approximate unity, confirming linear behavior. Conversely, R^2 values for the 95 to 140°C temperature suggest non-linear behavior. CTEs are found to be also considerably higher in the higher temperature range, which presumably is caused by greater polymer chain mobility above T_g.

Table 2. Calculated CTE from 2nd and 3rd cycle of cooling down procedure at different temperature ranges.

Sample orientation	2nd cooling cycle				3rd cooling cycle			
	40-95°C		95-140°C		40-95°C		95-140°C	
	CTE (10^{-6} K^{-1})	R^2 (/)	CTE (10^{-6} K^{-1})	R^2 (/)	CTE (10^{-6} K^{-1})	R^2 (/)	CTE (10^{-6} K^{-1})	R^2 (/)
0°	66	0.996	156	0.973	65	0.998	123	0.980
45°	63	0.998	142	0.990	62	0.998	114	0.977
90°	54	0.998	113	0.986	54	0.998	94	0.975

From XRD testing, the filler alignment was explored based on the filler crystal. A schematic of the (006), (105) and (204) lattice planes and recorded XRD patterns in the 0°, 45° and 90° specimen orientation are depicted in Fig.5(a) and (b), respectively. The ratio of the relative intensities between (006) and (105) (i.e., $(I(006))/(I(105))$) is often used to assess NdFeB orientation [7-8]. As shown in Fig.5(b), a decrease in intensity ratio was ascertained with increasing specimen deviation from the alignment direction, i.e., 5.76 to 3.98 for 0° to 90°, which confirms the alignment of the magnetic filler and corresponding decrease in CTE as mentioned above.

4 Conclusions

In this study, aligned composites comprising 12vol% anisotropic magnetic NdFeB particles and a modified epoxy polymer matrix were successfully fabricated via a jig comprising a Halbach array with magnetic field strength of 0.3T. CTEs were measured experimentally via heated stage and optical extensometer for specimen orientations 0°, 45° and 90° from the magnetic field direction. Data for three heating and cooling cycles were recorded for a temperature range of 40 to 140°C. It was observed that CTE data was noisy for the heating cycles and varied notably between the first and the subsequent cycles, leading to the conclusion that post-curing effects in polymer matrix occurred in the first cycle. Hence, CTE data was analyzed for the cooling process omitting the first cycle. From DSC testing, the T_g of samples was measured as 92.6°C, leading to the definition of two temperature ranges for this study, i.e., 40-95°C and 95-140°C. A linear thermal expansion behavior was ascertained for the 40-95°C range whereas the response was found to be non-linear for the higher temperature range. Also, CTEs were observed to be substantially greater for the higher temperature range, by a factor of 1.74 to 2.36 depending on specimen orientation and cooling cycle. The study of the filler crystal structures in fabricated composites via XRD analysis confirmed sample anisotropy in terms of particle alignment, which corroborates the observed anisotropy in terms of the produced samples' thermal expansion behavior.

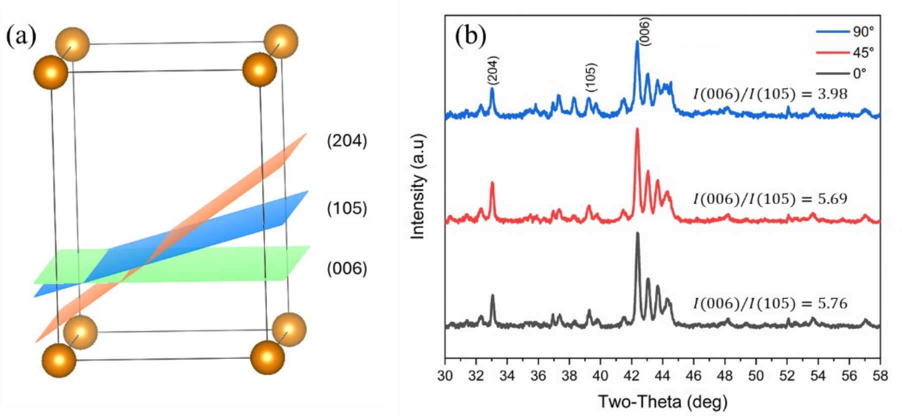

Figure 5. (a) Schematic of NdFeB crystal lattice planes, and (b) XRD traces for 0°, 45° and 90° specimen orientations.

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