

PREPARATION AND PROPERTIES OF STEPWISE GRADED SYNTHETIC GRAPHITE/PHENOLIC NANOCOMPOSITES

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Abstract

Stepwise, functionally- graded synthetic graphite/phenolic nanocomposites (FGNs) were fabricated using a combined powder stacking and compression moulding techniques. Ball milling was used to homogeneously distribute synthetic graphite within the phenolic resin matrix. The process allowed FGNs with four different microstructure gradient patterns of the same geometry and graphite content, as well as non-graded nanocomposites (NGNs), to be fabricated. It was found that the thermal properties of nanocomposites could be manipulated by changing the gradient patterns.

1 Introduction

Functionally graded materials are advanced composites with a gradient microstructure (and thus also graded properties), and have extensive applications in the aerospace engineering and automotive industry [1]. Functionally- graded metal and ceramic composites have been widely analyzed, fabricated, and characterized [2]. The concept of functionally graded structure has been applied to polymeric matrix composites. Functionally graded epoxy based composites have been fabricated with different reinforcements such as carbon fiber [3], silicon carbide [4], glass [5], and other polymers such as polyurethane [6]. Nano-scale reinforcements have also been used to fabricate functionally graded ceramic and metallic based nanocomposites. Recently, Estili et al. [7] fabricated functionally graded carbon nanotube ceramic matrix composites by a spark plasma sintering process. Kwon et al. [8] have reported the fabrication of functionally graded carbon nanotube metallic matrix composite using a powder metallurgy technique. However, functionally graded nano-scale reinforced composites with polymeric matrices have not yet been reported.

In general, polymer nanocomposites have been shown to be able to exhibit excellent mechanical, thermal, electrical, and physical properties. For example Li et al. [9] fabricated poly(vinylidene fluoride)/graphite nanoplatelet composites using solution mixing and compression molding method and reported great enhanced in both conductivity and dielectric constant. The epoxy/graphite composites showed improved tensile properties with increasing filler content [10]. It has been reported that graphite epoxy composites have high mechanical properties in cryogenic environments [11]. Rafiee et al. [12] reported that addition of only 0.1% weight fraction of graphene platelets into the epoxy matrix significantly increased the critical buckling load. It has been also found that carbon nanotube epoxy nanocomposites have outstanding mechanical [13], thermal [14], electrical [15], and fatigue properties [16].

Multiwall carbon nanotube reinforced epoxy were able to demonstrate good mechanical properties in cryogenic environments [17]. Despite the excellent properties of most conventional nanocomposites, their engineering and structural applications are restricted due to high production cost of nano-scale reinforcing materials. Therefore, an optimization in design of conventional nanocomposites is required to fully take advantage of their excellent properties. In this study, we demonstrate the design and fabrication of functionally graded polymer based nanocomposites by powder stacking and compression molding of phenolic resin mixed with synthetic graphite. Four different gradient patterns and non-graded nanocomposites with the same thickness and total synthetic graphite content were fabricated.

2 Materials and methods

The thermosetting phenolic resin with 9% hexamethylenetetramine (HMTA) as curing agent was obtained from Hexion Specialty Chemicals Pty Ltd. Synthetic graphite nano-platelets (SG) with average thickness of 100 nm and diameters of 1-3 μm were supplied by Asbury Graphite Mills, and are products of the heat treatment of carbonaceous materials with 99% purity and density of 1.75 g/cm³, and have highly exfoliated and crystalline structure. The SG nano-platelets were dried in a vacuum oven at 40°C for 24 hours to remove moisture contents. The powder mixtures of SG and phenolic resin with 5,10, and 20wt% SG contents were ball milled (8000M, Mixer /Mill, Maker, Spex, USA) for 1 hour to ensure homogeneous dispersion of SG within the phenolic resin. All samples were fabricated using compression molding and powder stacking technique. Premixed composite powders of certain SG contents were settled in a die of a hot press in a desired sequence using a stacker device. The graded stacks of composite powders heated up to 130°C for 10 minutes and then hot pressed at 180°C and 15 MPa for 10 minutes and finally cooled down. A range of compositions were made. As shown in Figure 1 FGN-1 has the concentration of SG decreasing from the outer surfaces to the core from 20 to 0wt%. In contrast, FGN-2 has 20wt% SG in the core and neat phenolic resin layer on the top and bottom. In FGN-3, the SG content decreases from 20wt% on the top layer to 0wt% on the bottom layer. FGN-4 has a reverse compositional change, in comparison to FGN-3. NGNs are isotropic homogenous single layer samples with the average mass fraction of SG in FGNs (i.e. 8.75wt %).

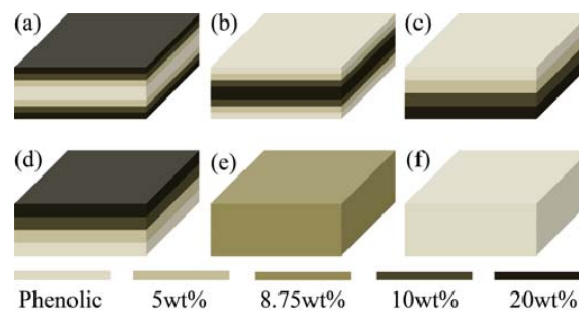


Figure 1. Schematic illustration of the samples (a) FGN-1, (b) FGN-2, (c) FGN-3, (d) FGN-4, (e) NGN, and (f) Phenolic

Optical macroscopy was used to investigate the cross section of different configurations of FGNs using Olympus SZX12 digital camera coupled with an Olympus DP70X optical microscope. To allow imaging, the samples were mounted in casting resin, ground using three different grit silicon carbide papers on a Struers polishing and then polished on a MD-Mol, MD-Nap and MD-Chem surface with the abrasive types of DP-Susp, p 3 μm , DP-Susp, p 1 μm and OP-S, 0.04 μm , respectively. The thermal conductivity of individual layers was measured with the C-Therm Thermal Conductivity Analyzer employing the modified transient plane source (MTPS) technique. The thermal expansion of each layer of the FGNs was measured according to ASTM E831 using a thermal mechanical analyzer (TMA) equipped with a quartz dilatometer (Perkin Elmer DTMA7). The specimens were inserted in

a furnace and then heated to 100°C at a heating rate of 5°C/min. All expansion measurements were performed using an expansion probe under a constant flow rate of 35 cm³/min of helium gas and an applied static force of 300 mN.

2 Results and discussion

The morphology and distribution of SG within the matrix was investigated using the scanning electron microscopy. Figure 2 shows the SEM micrographs of the individual layers of the freshly cut samples. The SGs were uniformly distributed within the matrix, even at a very high SG concentration (i.e. 20wt %) and no agglomerated or clustered SG was observed. This suggests that the ball milling method is highly effective procedure in homogeneously dispersing SGs in phenolic matrix.

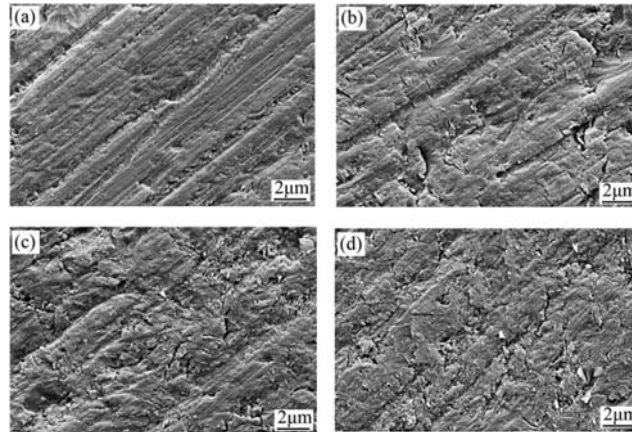


Figure 2. SEM micrograph of (a) neat phenolic and its nanocomposites with: (b) 5wt% SG, (c) 10wt% SG, and (d) 20wt% SG

The optical macrographs of the polished cross-section of the FGNs with four different gradient patterns are shown in Figure 3. The layers were homogeneous and had clear interlayer boundaries. This layer by layer stacking enabled the microstructure and composition over the thickness to be controlled and resulted in 600 µm thick individual layers. Despite high concentrations of SG, no interlayer defects, delamination or cracking was observed. This can be attributed to the excellent thermo-mechanical match between the layers and gradual variation in microstructure and thermo-mechanical properties, and is an advantage of using nanocomposites where lower concentrations are required, compared to microcomposites.

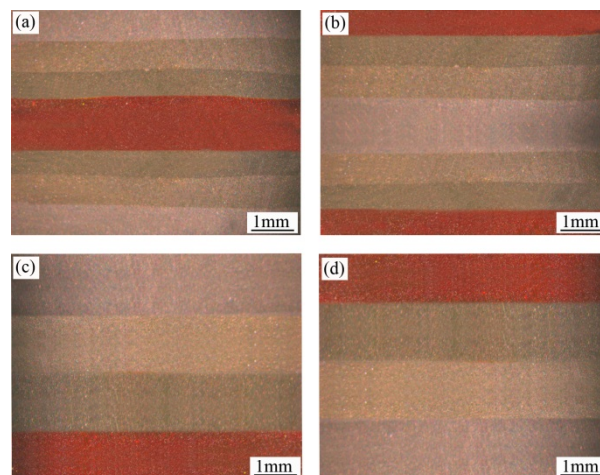


Figure 3. Optical macrograph of the polished cross-section of the stepwise gradient FGNs: (a) FGN-1, (b) FGN-2, (c) FGN-3, and (d) FGN-4

The coefficient of thermal expansion of the individual layers was calculated from the slope of the thermal expansion-temperature graph in the range of 25–100°C [18] and is presented in Fig. 4. CTE decreased 10.56, 17.95, and 23.05% by introducing 5, 10, and 20wt% SG into the phenolic matrix. This gradient in CTE over the thickness, as a result of gradient structure, induces residual thermal stress during the cooling period of the fabrication process [19]. In the case of FGN-1, the increase of CTE from the top and bottom surfaces to the core results in conception of compressive residual thermal stress between the layers during the fabrication process, which prevents delamination due to high tensile stress within the inner layers and increases the load bearing capacity of the structure [20].

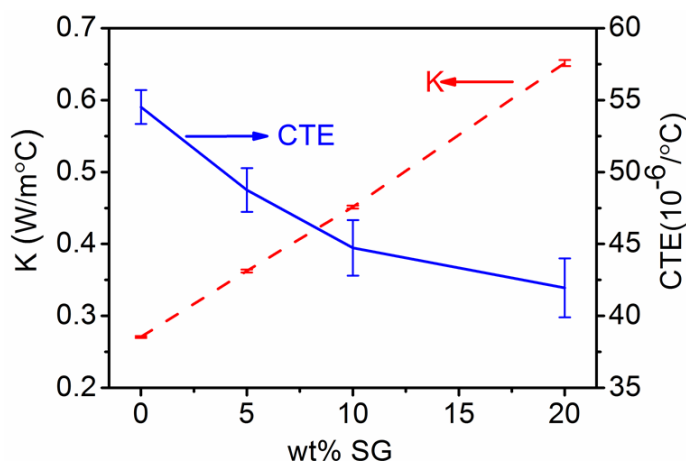


Figure 4. Thermal conductivity and heat capacity of individual nanocomposite layers

The thermal conductivity of the individual layers is also presented in Fig. 4. Thermal conductivity increased continuously with increase in SG content. In comparison with phenolic, its nanocomposites showed improved thermal conductivity at. Depending on the SG content, the enhancement varied from 33.87% (nanocomposites with 5wt% SG) to as high as 140.06% (nanocomposites with 20wt% SG) at room temperature. The small standard deviations of thermal conductivity of the samples indicate that SG is uniformly distributed within the matrix. The low thermal conductivity of thermosetting polymers makes them suitable for applications in environments where temperature control is required such as in thermal insulation. However, due to their low thermal conductivity, the time required for the entire body of the structure to reach the equilibrium temperature is relatively long, which may cause severe temperature gradient between the surface and the core in such thick samples. This creates residual thermal stress and decreases the service life of the structure. However, an in-depth gradient of thermal conductivity in the type of structures reported here can be responsible for decreasing the thermal stress in thermal environments [21].

Conclusions

We have fabricated functionally graded synthetic graphite/phenolic nanocomposites using a powder stacking technique and compression molding. The controlled microstructure and composition were achieved in micrometer scale. A well-defined boundary between the layers was observed with no interlayer defects or cracking. Uniform distribution of high SG contents in phenolic resin was obtained by ball milling technique and no agglomeration was observed. Thermal conductivity and coefficient of thermal expansion were able to be controlled by controlling the composition across the thickness.

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