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AC and DC electrical properties of graphene nanoplatelets reinforced epoxy syntactic foam*

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Abstract

Benefits of employing graphene nanopletlates (GNPLs) in composite structures include mechanical as well as multifunctional properties. Understanding the impedance behavior of GNPLs reinforced syntactic foams may open new applications for syntactic foam composites. In this work, GNPLs reinforced syntactic foams were fabricated and tested for DC and AC electrical properties. Four sets of syntactic foam samples containing 0, 0.1, 0.3, and 0.5 vol% of GNPLs were fabricated and tested. Significant increase in conductivity of syntactic foams due to the addition of GNPLs was noted. AC impedance measurements indicated that the GNPLs syntactic foams become frequency dependent as the volume fraction of GNPLs increases. With addition of GNPLs, the characteristic of the syntactic foams are also observed to transition from dominant capacitive to dominant resistive behavior.

Introduction

Syntactic foams are particulate composites containing hollow microballoons and a polymer binder. The microballoons are added to provide closed cell porosity and reduce the density of the composites. Syntactic foams have high specific strength, high bending stiffness, low thermal and electrical conductivities, and low moisture absorption [1]. They have wide range of possible applications in aerospace, automotive, and marine sectors. Several studies have been conducted in order to improve the physical and mechanical properties of syntactic foams to attain specific properties [2, 3]. In order to improve the properties of the foams, various types of short fibers have been used to reinforce the syntactic foam matrices. For example, glass and aramid fiber bearing syntactic foams have been used to improve compressive strength and modulus properties of syntactic foams [4–6]. The addition of short glass fibers has also significantly increased the flexural strength and modulus of syntactic foams [7, 8]. Incorporation of carbon fibers in syntactic foams was also found to considerably increase the ultimate tensile strength and modulus of the foams [9]. Nanoparticles generally pose very high surface energy due to their nano scaled size and can interact with the polymer chains better than microsized fiber fillers and improve the matrix properties significantly. Studies indicated that incorporation of only 2%–5% nanoclay particles into syntactic foam enhances the energy absorption properties of the foams [10]. A considerable improvement in the mechanical properties such as tensile, flexural, and compressive strengths and corresponding moduli was also observed for the foams on incorporation of nanoclay [11].

Conductive nanofillers such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have properties that are unrivaled by any other nanofillers. Especially, their specific stiffness and conductivity makes them an attractive fillers to tailor the properties of low density composites such as syntactic foams. Very few studies have reported the use of these conductive nanofillers in syntactic foams [12–16]. In order to use the advantages of these conductive fillers, we have developed a technique by growing the CNTs/CNFs on the microballoons surface [17–20]. Some researchers pursued this technique to improve the mechanical, thermal and electrical properties of syntactic foams [21]. Most of these reports focused on the mechanical and thermal properties study

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of the foams. Large scale synthesis, purification, and dispersion of these nanofiber fillers in syntactic foams are still far from being achieved. Consequently, study of electrical properties of carbon nanofillers reinforced syntactic foams is scant.

Graphene platelets (GNPLs) are novel potential fillers with two-dimensional graphene thin plates containing few layers of graphene sheets. They have excellent performance characteristics and can replace carbon nanofibers. They have high surface area than carbon nanostructures that provide stronger filler-matrix adhesion, thus maximizing the stress transfer [22]. GNPLs are also currently being produced in bulk quantities with low cost [23]. These nano-materials have been used as fillers in polymeric composites to tailor the mechanical properties and produce high performance composites [22]. Comparative study on the mechanical properties of epoxy nanocomposites with GNPL, single-walled CNT (SWCNT), and multi-walled CNT (MWCNT) additives has been done at a filler weight fractions of $0.1 \pm 0.002\%$ [24]. Results indicated that GNPLs significantly out-perform CNT additives [24]. It was observed that addition of very low volume fraction of GNPLs improved the tensile modulus, tensile strength, fracture toughness, and fracture energy properties of the polymer composite compared to the plain (no-fillers) composite. The effect of these novel fillers on the mechanical properties of syntactic foams has also been reported [25]. Studying the electrical properties of GNPLs reinforced syntactic foams (GNPLs-SF) could provide useful information about their microstructures, frequency dependent of their electrical properties, and can help investigating their possible applications in electronics. To the best of our knowledge, studies on electrical impedance properties of GNPLs-SF is not available. This paper discusses direct current (DC) and alternating current (AC) electrical properties of GNPLs-SF composites containing different volume fraction of GNPLs.

Fabrication of GNPLs syntactic foam

Pristine GNPLs used in this study were obtained from Cheap Tube Inc. According to the specifications provided by the company, they have <4 layers, diameter of 1–2 μm, thicknesses of <5 nm, and surface area of 700 $m^2 g^{-1}$. The hollow glass microballoons used were supplied by 3M Company under the trade name of S38. These microballoons are high-strength polymer additives made from chemically-stable soda-lime-borosilicate glass. When these microballoons added in a polymeric system, they provide closed cell porosity and reduce the density of a composite. The epoxy matrix for the fabrication of the syntactic foams comprised a high purity bisphenol A diglycidylether resin and an economical aliphatic polyamine hardener, triethylenetetraamine (TETA), both obtained from Dow Chemical Company, USA. Syntactic foams containing 0.1, 0.3, and 0.5 vol% of GNPLs were fabricated for this study. The GNPLs were first dispersed in toluene and sonicated for 5 s. Epoxy was then added to the toluene/GNPLs suspension and mixture was then sonicated for additional 10 min. The sonicator was adjusted to pulse on for 10 s and off for 5 s with the amplitude set at 40%. Afterwards, the mixture was kept in degasing chamber at 60 °C to remove the toluene. Thereafter, glass microballoons and the hardener were added, and the mixture was poured into a mold prepared from Dow corning 3120 RTV silicon rubber. The samples were allowed to cure at room temperature for 24 h and post cured at 100 °C for 3 h. Neat syntactic foam samples that did not contain GNPLs were also fabricated. The volume fraction of microballoons in all fabricated samples was 30%.

Characterization methods

Scanning electron microscope (SEM) (FEI Quanta 3D FEG Dual Beam FIB/SEM) and transmission electron microscope (TEM) (JEOL JEM-1011 TEM) were used to study the GNPLs dispersion in syntactic foams. For SEM characterization, samples were sputter coated with thin gold layer before imaging to make their surface conducting.

Electrical measurements, DC and AC, were performed using SI1287 electrochemical interface and 1252 A frequency response analyzer (AMETEK, Inc.). Z-view software was used to maximize the performance and data handling of the system. Measurements were performed in the frequency range of 100 Hz to 0.3 MHZ for all the GNPLs reinforced syntactic foams and at room temperature (23 °C). For DC measurements, the voltage was varied from −10 to 10 V and the current passing across the thickness of the sample was recorded corresponding to the applied potential. In order to realize ohmic contacts with the electrodes, conductive PELCO conductive Silver 187 (Ted Pella, Inc.) was applied uniformly on opposite faces of the samples (5 mm × 5 mm × 1.5 mm) and a lead wire was affixed to these surfaces using the silver paste.

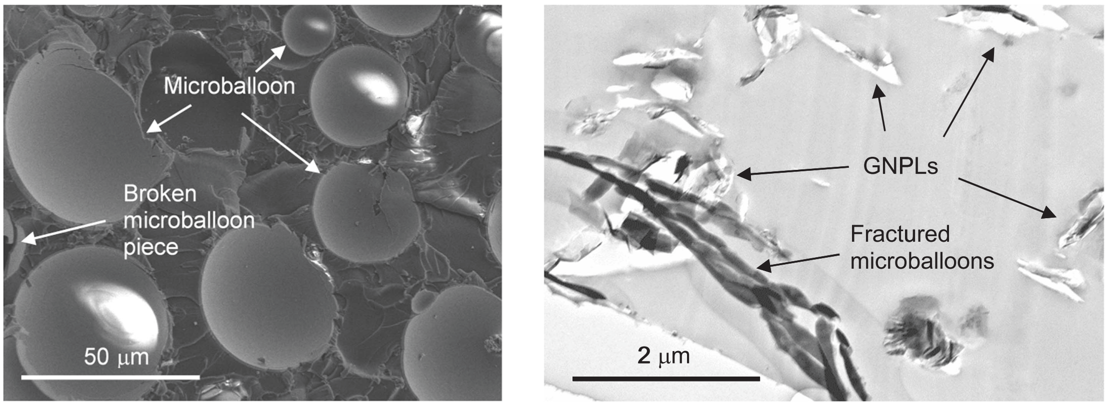

Figure 1. (a) SEM and (b) TEM micrographs of samples containing 0.3 vol% GNPLs.

Results and discussions

The SEM image of a fractured sample (0.3 vol% GNPLs) is shown in figure 1(a). It can be seen that the glass micoballoons have a wide variation in diameter. Typically, the diameter of the microballoons varies between 5 μm to 100 μm. There is also a large variation in the wall thickness, ranging between few hundred nanometer to few micrometer (1–4 μm) [26], and this variation is in the range of the dimensions of GNPLs. As it can be seen in figure 1(a), a fractured glass microballoon piece on the sample surface appeared to have two dimensional geometry similar to the GNPLs. Hence, it was difficult to differentiate the fractured glass pieces from the GNPLs. In the case when the GNPLs embedded in the matrix, due to their planar geometry, only the edges of the GNPLs embedded in the matrix were exposed. Since the GNPLs were embedded in the resin, the thickness would likely increased and could approach the thickness of the microballoons. As a result, distinguishing the platelet edges from the edges of fractured microballoons was extremely difficult. Therefore, attempts to study the dispersion of the GNPLs in syntactic foams using SEM were not successful. Although it was possible to distinguish the GNPLs from microballoon fragments using TEM (figure 1(b)), it was challenging to accurately determine the GNPLs dispersion as the areal coverage of the TEM grid was too small and reliable statistics could not be derived. The TEM study, however, did not show aggregation of the GNPLs in the samples. The dimensions of the GNPLs observed under TEM study, in any direction, were generally less than 2 μm, which falls within the diameter of the GNPLs. However, some GNPLs rolled to form voids in the 0.5 vol% GNPLs containing sample. The effect of this void will be discussed later.

The current density versus electric field plots of the fabricated samples are shown in figures 2(a) and (b). For all samples, the current density increases linearly as the applied field increases. The sample with a greater slope is a better electric conductor than the material with a lesser slope. The inverse of the slopes of these curves give the volume resistivities of the samples. Figure 2(c) shows the plot of the resistivities of the samples against the volume fractions of the GNPLs. As it can be observed from the figure, the resistivities of the samples go through a large change at volume percentages of the GNPLs, indicating the partial formation of interaction between adjacent GNPLs. It can be noted that the resistivity of the foams significantly reduced to 3.19×10^5 Ωm with addition of 0.5 vol% GNPLs, making the syntactic foam suitable for electrostatic dissipation applications [27–29]. There is five orders of magnitude difference between the resistivities of the neat syntactic foam and the sample containing 0.1 vol% GNPLs. However, when more GNPLs added, the effectiveness in reducing the resistivity of the syntactic foam decreases. Specifically, the change in resistivities between samples containing 0.3 and 0.5 vol% is comparatively lower. During the TEM study, since agglomeration of the GNPLs was not observed in samples containing 0.1 and 0.3 vol% GNPLs, it is reasonable to attribute the significant decrease in the resistivity of the samples to the homogeneous dispersion of the GNPLs to form conducting paths to enable electron tunneling in the syntactic foams. Although the addition of 0.5 vol% GNPLs decreased the resistivity, the magnitude of resistance change from the 0.3 vol% sample is relatively small. This has been attributed to the percolation threshold phenomenon of the fillers in the matrix [30, 31]. It can also be seen from the TEM image of the sample (figure 2(d)) that the GNPLs rolled or wrapped to form voids at higher volume fraction, possibly due to the high shearing action during mixing, which further contributes to the decrease in the additional fillers effectiveness.

Figures 3(a) and (b) show the Bode diagrams of the samples with different volume fractions of GNPLs. As it can be noted from figure 3(a), at low volume fraction of GNPLs, the impedance of syntactic foams decreases with frequency. This indicates that the reactive part of the impedance for low volume fraction of GNPLs is

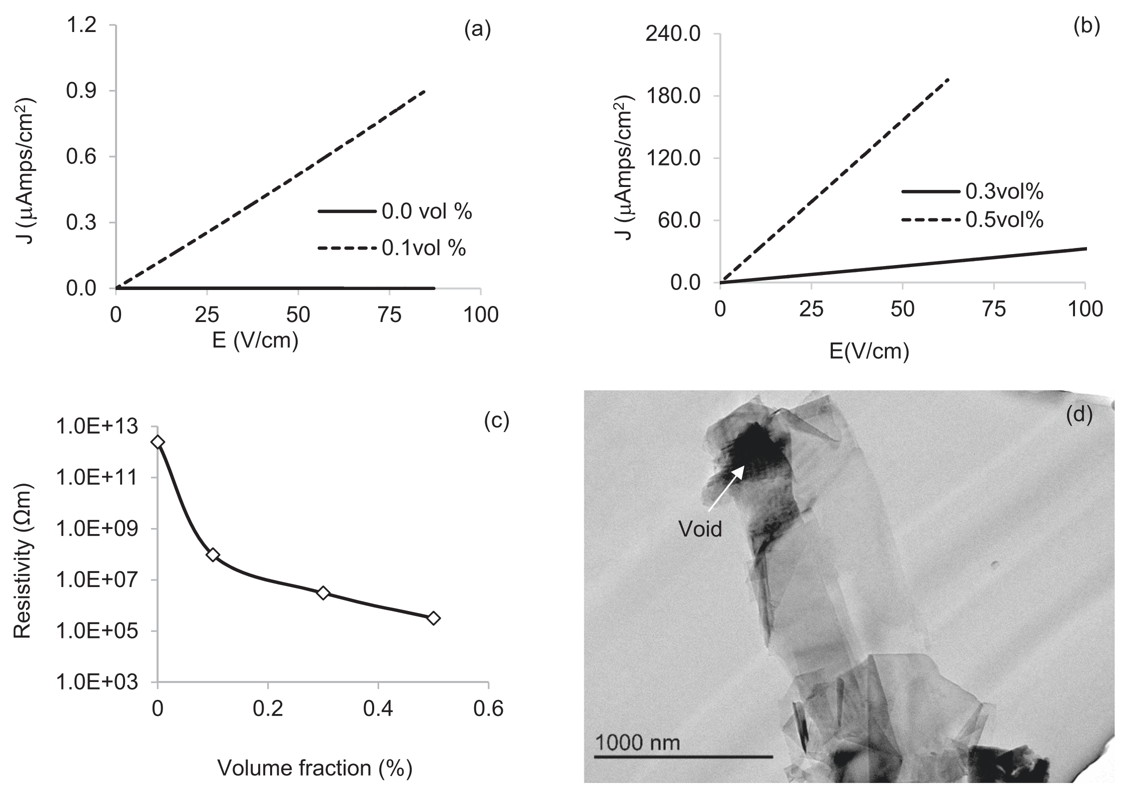

Figure 2. (a) and (b) are current density (J) versus electric field (E), (c) resistivity versus volume fraction of GNPLs, and (d) TEM of 0.5 vol% sample.

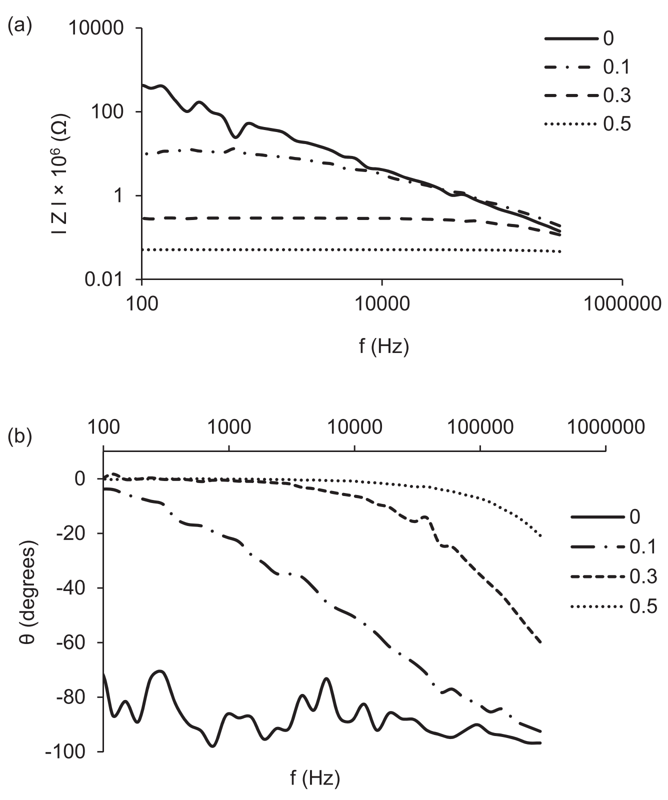

Figure 3. (a) Magnitude of impedance and (b) phase angle versus frequency plots at different volume fraction of GNPLs.

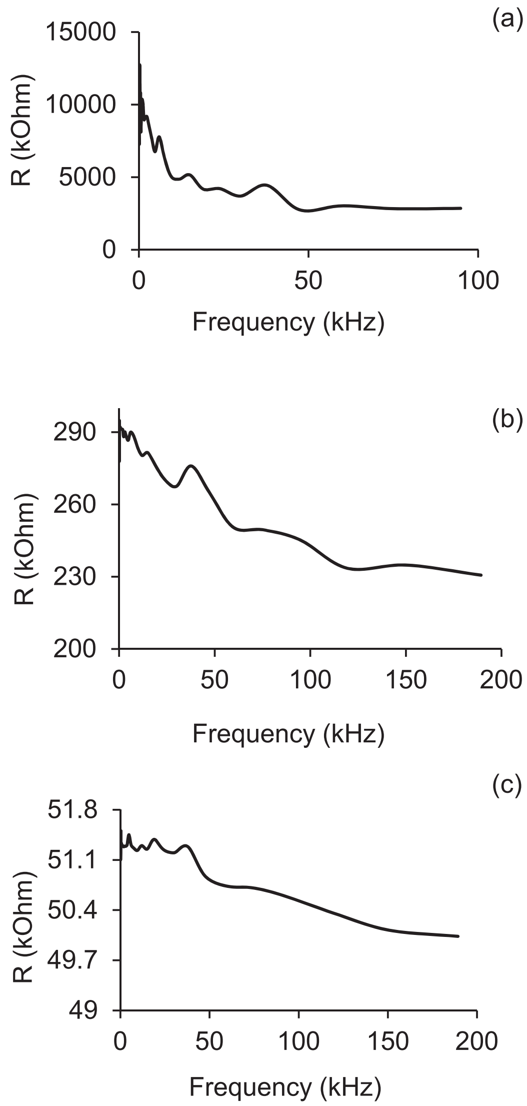

Figure 4. Variation of electrical resistance against frequency of syntactic foams containing (a) 0.1, (b) 0.3, and (c) 0.5 volume fraction of GNPLs.

predominantly capacitive. As the volume fraction increases from 0 to 0.5 vol%, the impedance of syntactic foams become frequency independent. This implies that the characteristics of the syntactic foams transitioned from dominant capacitive to dominant resistive materials as the volume fraction varies from 0 to 0.5%. As it can be seen in figures 3(a) and (b), when no GNPLs are added in the foams, the logZ-log$f$ curve is a straight line while the phase angle θ is negative and converges to $-90°$ as the frequency increases, becoming an ideal capacitor ($Z \approx 1/(2\pi fC)$). Whereas the impedance magnitude of samples containing 0.3 and 0.5 vol% of GNPLs are close to being frequency independent with the phase angle θ approaches $0°$, at lower frequency, indicating a characteristics of a resistive materials. However, as the frequency increases, a slight drop in the impedance magnitude was observed. The phase angle θ also diverted from $0°$ and becomes negative. These changes are attributed to the influence of a parallel capacitance across the samples. Based on figures 3(a) and (b), capacitive to resistive transition is significant with addition of 0.1 vol% GNPLs. The addition of this volume fraction of GNPLs resulted a five order reduction in resistivity of the syntactic foam when compared to a plain samples. This was due to the partial formation of conductive pathways by the GNPLs particles. With increase in the volume fraction of the GNPLs, the interaction between the conductive particles increases. This increases the resistive coupling of current between the particles. Consequently, the syntactic foams changed from capacitive to resistive characteristics [32]. After addition of 0.3 vol% of GNPLs, the resistive coupling between the GNPLs particles was the main reason for the AC conduction and the syntactic foam behaved like a semiconductor. However, the impedance values are quite high at all frequency, which attributed to weak contacts between GNPL particles. In addition, the impedance showed a slight frequency dependence at higher frequency. This might be attributed to the capacitive effects generated due to the thin dielectric layers between the conductive GNPL particles.

Figure 4 shows the variation of electrical resistance against frequency of GNPLs containing samples. Similar behavior is observed in all samples. At lower frequency, the AC resistance of all the samples is frequency dependent, decreasing with frequency. At higher frequency, the samples tend toward frequency independent. However, there is significant difference in the variation of the range of the resistance of the samples. When the volume fraction of GNPLs is 0.1, the resistance decreases an order of magnitude as the frequency increases. As more GNPLs added into the syntactic foam, the range in which electrical resistance varies against the frequency becomes narrowed. Consequently, the resistance becomes more stable with frequency, a behavior of semiconducting and conductive materials.

Conclusions

The impedance properties of graphene nanoplatelets reinforced syntactic foam samples are investigated. Volume fractions of nanoplatelets varying from 0 to 0.5% were used to fabricate the samples. It is observed that increasing the volume fraction of GNPLs changed the syntactic foams from insulating to semiconducting material. The transition was significant when 0.1 vol% GNPLs are added into the matrix. The study investigated that at lower volume fraction of GNPLs, the impedance magnitude showed a strong dependence on frequency in the lower range, dominated by the capacitive effect. Whereas at higher volume fraction, the impedance was almost constant at lower frequency and showed little dependence with frequency, dominated by the resistance of the material.

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