Multifunctional epoxy composites modified with a graphene nanoplatelet/carbon nanotube hybrid

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Abstract
Epoxies are a class of thermoset polymers which find use in high performance applications. However, epoxies are inherently brittle and are poor conductors of electricity, which limits their ability to be employed in functional applications. Carbon nanomaterials have attracted considerable attention as filler materials, due to their combination of outstanding properties. In the present work, an epoxy polymer was modified with a hybrid nanofiller, consisting of graphene nanoplatelets (GNPs) and carbon nanotubes (CNTs) at a mass ratio of 9:1, using three-roll milling. Addition of 1 wt% resulted in an increase of eight orders of magnitude in the electrical conductivity and a 182% increase in the fracture energy, $G_{IC}$, of the epoxy. CNTs contributed greatly in the reduction of the percolation threshold, which was 10 times lower than that of conventional GNP/epoxy composites, while the increase in toughness was entirely attributed to the GNPs, predominantly through the mechanism of crack deflection. The toughening contribution of the hybrid nanofiller was theoretically calculated using analytical modeling, which showed excellent agreement between the predicted and experimental values of $G_{IC}$.

KEYWORDS
graphene, mechanical properties, microscopy, nanotubes, thermal properties, thermosets

1 | INTRODUCTION

Epoxy resins are thermoset polymers, which are characterized by the formation of a three-dimensional, cross-linked network following polymerization. Epoxy polymers benefit from high strength and modulus, good thermal and chemical resistance, and as such they are extensively used as matrices in fiber-reinforced composites and adhesives in the aerospace and automotive industries, where the application of high-performance lightweight structures is highly desirable. Despite their apparent advantages, epoxies suffer from certain limitations. They are poor conductors of both heat and electricity, are inherently brittle and suffer from low toughness. The above considerations limit the widespread application of epoxy polymers in high performance components. Addition of filler materials into the epoxy matrix is a very effective method of fabricating advanced composite materials, which combine the advantages of both the matrix and filler. Carbon nanomaterials, including graphene and carbon nanotubes (CNTs) have emerged as key filler materials for the development of multifunctional epoxy composites due to their superior mechanical, thermal and electrical...
properties compared to traditional fillers, such as core-shell rubber,\textsuperscript{1} silica,\textsuperscript{2} alumina,\textsuperscript{3} and clay particles.\textsuperscript{4}

CNTs have attracted significant attention as reinforcing agents in polymers, due to a combination of highly attractive mechanical and electrical properties.\textsuperscript{5} CNTs are the one-dimensional allotrope of carbon and can be thought of as rolled sheets of graphene. Improvements in the mechanical, fracture and electrical properties of epoxy polymers have been reported with addition of CNTs.\textsuperscript{5–8} Most importantly, the percolation threshold of CNT-modified epoxies is considerably lower than for composites containing conventional conductive fillers, such as metallic particles (i.e., Cu, Ag) or carbon black (CB), because of the very high aspect ratio of CNTs. The percolation threshold for CB in epoxies is typically 1 wt %,\textsuperscript{8} for metallic fillers this normally exceeds 60 wt%,\textsuperscript{7} while for CNT/epoxy composites this varies between 0.002 and 0.1 wt%.\textsuperscript{5,7} The high aspect ratio of CNTs is also thought to help them act as an effective secondary reinforcement in multiscale composites, whereby they are thought to bridge the fiber reinforcement to the matrix resulting in more efficient load transfer compared to typical fiber-reinforced plastics.\textsuperscript{9}

The two main types of graphene fillers used in composite applications are based on: (a) graphite intercalation compounds (GICs) and (b) graphene oxide (GO). GO contains oxygen-containing functional groups on its surface, which enables the preparation of GO-reinforced epoxies with very good mechanical and thermomechanical properties owing to the exceptional interfacial interaction between GO and epoxy.\textsuperscript{10–12} However, the major drawback associated with the use of GO is its electrically insulating nature, which arises from the disruption of the sp\textsuperscript{2}-hybridized lattice as a consequence of the oxidation process.\textsuperscript{13,14} On the contrary, graphene nanoplatelets (GNPs) are derived from GICs and possess sp\textsuperscript{2}-graphitic structure; hence constituting a promising candidate for improving the electrical conductivity of epoxy polymers. GNPs are an ultra-thin form of graphite, consisting of more than 10 graphene layers but not exceeding thicknesses of 100 nm.\textsuperscript{15} They represent one of the thinnest graphene compounds produced at industrially scalable quantities and already find application in advanced sports equipment, as for example in graphene-reinforced tennis racquets.\textsuperscript{16} The incorporation of GNPs to epoxy matrices results in an increase in the Young’s modulus of the resulting composite material but does have a negative effect on the tensile strength.\textsuperscript{17–20} Moreover, the addition of GNPs has a reinforcing effect on the fracture toughness ($K_{IC}$) and fracture energy ($G_{IC}$) of epoxy polymers.\textsuperscript{17,18,20–22} The use of GNPs has a positive influence on the electrical properties of epoxy polymers and can improve the bulk electrical conductivity of epoxies by 7–9 orders of magnitude at filler loadings above the percolation threshold.\textsuperscript{20,22–24}

An approach which has gained prominence is the combination of nanomaterials of different shapes, as in the case of GNP/CNT hybrids, where CNTs have the ability to bridge adjacent GNPs resulting in the formation of three-dimensional conductive networks.\textsuperscript{24} GNP/CNT hybrid composites exhibit improved mechanical properties due to a superior state of dispersion, whereby the stacking of platelets is inhibited by the presence of the CNTs.\textsuperscript{25} Yang et al.\textsuperscript{25} determined the mechanical properties of epoxy composites modified respectively with 1 wt% of CNTs, GNPs and a GNP/CNT hybrid of 9:1 mass ratio and found that the hybrid nanofiller exhibited an improved reinforcing effect compared to the CNTs and GNPs alone. This resulted in increases of 23% in the Young’s modulus (from 2.65 GPa) and 15% in the tensile strength (from 48 MPa). Regarding fracture properties, Chatterjee et al.\textsuperscript{26} investigated the effect of the GNP:CNT ratio on the fracture toughness, $K_{IC}$, of epoxy composites for a total filler content of 0.5 wt%, and concluded that the greatest improvement in $K_{IC}$ was seen for the highest CNT content hybrid, of 1:9 mass ratio, measuring an increase of 76% with respect to the unmodified epoxy (from 0.5 MPa m\textsuperscript{1/2}). Yue et al.\textsuperscript{27} reported that a hybrid nanofiller of GNPs and CNTs at a mass ratio of 2:8 synergistically contributed to a reduction of the electrical percolation threshold in epoxy composites. It was reported that the hybrid nanofiller demonstrated a reduced percolation threshold ($p_c$) of 0.62 wt% in contrast to the CNT and GNP single-filled composites, which exhibited $p_c$ values of 0.84 and 0.88 wt%, respectively. This was attributed to the more efficient formation of conductive pathways between the nanocarbon particles. On the contrary, Huang et al.\textsuperscript{28} did not observe any synergy effects, with the electrical conductivity values of the CNT-filled epoxies consistently outperforming those of the GNP/CNT hybrid (at a volume ratio of 1:1), at various volume fractions.

However, from the above references in the literature regarding the use of GNP/CNT hybrid fillers in epoxy resins it becomes apparent that findings are not consistent and no mechanistic explanation is provided with regards to which species and why contributes most to the improvement in properties. Moreover, the presence of synergy is contradicted among different authors and in the works where synergy is observed, the reported ratios vary significantly with no attempt from the authors to explain why synergetic effects occur. In the present work, we attempt to study the effect that a hybrid nanofiller imparts on a wide range of properties of a commercial
aerospace grade epoxy and rationalize how the different species contribute to the reported improvements in electrical conductivity and fracture energy. Firstly, a range of GNP/CNT hybrid epoxy composites was prepared at a total filler content of 0.5 wt%, and the effect of the nanocarbon species ratio on the electrical conductivity of the composites was assessed. It was found that a 9:1 GNP/CNT ratio offered the best compromise between high electrical conductivity and good processability. The 9:1 hybrid was then incorporated into the epoxy resin at various loadings ranging from 0 to 1 wt%. The range was selected based on the criterion that the percolation threshold was expected to be found within that range and also, with the consideration that high nanocarbon loadings result in increasingly brittle composites with significantly reduced tensile strengths. The mechanical, thermal, electrical and fracture properties of the resulting composites were measured, and the effect of the nanofiller on the resulting properties was assessed. To the best of our knowledge, such an extensive characterization of GNP/CNT hybrid epoxy composites has never been undertaken in the past. A detailed fractographic examination was undertaken to assess the quality of dispersion and determine the toughening mechanisms. Finally, the toughening contribution of the two different nanofillers was predicted separately with the use of analytical models, and the combined contribution was then compared against the experimental values.

2 | MATERIALS AND MANUFACTURING

2.1 | Materials

An anhydride-cured epoxy polymer was used. A diglycidyl ether of bisphenol-A (DGEBA) liquid epoxy resin (Araldite LY556; Huntsman, UK) with an epoxide equivalent weight (EEW) of 185 g/eq was used. Graphene nanoplatelets (GNPs) with an average lateral size of 4.5 μm, average platelet thickness of 12 nm and surface area of 80 m²/g (Grade AO-3; Graphene Supermarket) were used. These GNPs were selected as they produced the most electrically-conductive epoxies in trials using a range of commercially-available GNPs. Multiwalled carbon nanotubes (MWCNTs) with an average length of 1.5 μm, average diameter of 9.5 nm and surface area of 250–300 m²/g (NC7000; Nanocyl, Belgium) were used.

2.2 | Manufacture of bulk epoxy polymers

The GNPs and CNTs were dispersed into the liquid epoxy resin by stirring using a spatula followed by three-roll milling (3RM). The epoxy/carbon nanofiller mixtures were passed through a three-roll mill (80E; EXAKT, Germany) eight times at a roller speed of 220 rpm and temperature of 40 °C. The roller gaps were set to 5 μm. The curing agent was added to the pre-dispersed resin and mixed with a mechanical stirrer (RZR 2012; Heidolph, Germany) fitted with a radial flow impeller at 500 rpm and 60°C for 15 min. The resulting mixture was degassed in a vacuum oven at −1000 mbar for a minimum of 30 min to remove all the air bubbles. The degassed mixtures were poured into preheated steel molds coated with release agent (Frekote 700NC; Henkel, Germany) and cured for 1 h at 90°C, followed by 2 h at 160°C in a fan oven. The molds were left to cool slowly to room temperature prior to the cured plates being removed.

3 | CHARACTERIZATION

3.1 | Thermal analysis

Dynamic mechanical thermal analysis (DMTA) was performed to determine the glass transition temperature (T_g) and storage modulus (E') of the bulk epoxy polymers using a Q800 analyzer (TA Instruments). Rectangular samples of 60 × 10 × 3 mm³ were cut from the cured bulk plates and tested in dual cantilever mode. The samples were subjected to a temperature sweep from 30 to 200°C at a heating rate of 2°C/min using a frequency of 1 Hz and an oscillation strain of 0.05%.

Thermogravimetric analysis (TGA) was carried out on the bulk epoxy polymers to determine their thermal stability using a TGA/DSC 1 analyzer (Mettler Toledo). Samples of 5–15 mg were placed in a platinum crucible and were heated from 30 to 800°C at a heating rate of 10°C/min in a nitrogen atmosphere (using a flow rate of 60 ml/min).

3.2 | Electrical impedance spectroscopy

Electrical impedance spectroscopy (EIS) was used to measure the electrical conductivity of the bulk epoxy polymers. Samples of 10 × 10 × 2 mm³ were coated on both surfaces with conductive silver paint and pressed between two capacitor plates in a two-electrode cell setup using a Reference 600 potentiostat (Gamry Instruments). The tests were conducted inside a Faraday cage to prevent electromagnetic interference, using a root mean
square alternating current (RMS AC) voltage of 10 mV over a frequency range of 100 mHz to 1 MHz.

3.3 | Mechanical tests

Tensile tests were conducted at room temperature using a universal testing machine (3369; Instron, UK), fitted with a 50 kN loadcell. Dumbbell specimens having a gauge length of 25 mm were machined from $75 \times 13.5 \times 3$ mm$^3$ strips cut from the bulk epoxy plates. A displacement rate of 1 mm/min was used, and the strain was measured using a clip-on extensometer (2620–601; Instron, UK). The Young’s modulus ($E_t$) was determined from the gradient of the stress versus strain curve between strains of 0.05% and 0.25%, according to ISO527-1.29 The tensile properties were averaged from the results obtained from a minimum of five specimens.

3.4 | Fracture tests

Single edge notched bending (SENB) tests were conducted to determine the fracture toughness ($K_{IC}$) and fracture energy ($G_{IC}$) of the bulk epoxy polymers, according to ASTM 5045.30 Test specimens with dimensions of $60 \times 12 \times 6$ mm$^3$ were used, and a 4 mm deep notch was machined in the center of the specimens using a horizontal mill. A sharp pre-crack was made by tapping a liquid nitrogen chilled razor blade into the notch. The tests were performed using an Instron 3366 universal testing machine (Instron, UK) fitted with a 10 kN loadcell. The specimens were loaded in three-point bending with a span of 48 mm, and a displacement rate of 1 mm/min was used. Following the conclusion of the SENB tests, the crack lengths were measured using an SMZ800 optical microscope (Nikon, UK). A minimum of 12 specimens were tested for each formulation.

The fracture energy ($G_{IC}$) was calculated from the measured $K_{IC}$ values using the linear elastic fracture mechanics (LEFM) approach, according to Equation (1):

$$G_{IC} = \frac{K_{IC}^2}{E_t (1-\nu^2)}$$

where $E_t$ is the Young’s modulus, and $\nu$ is the Poisson’s ratio, taken as 0.35, which is typical for an epoxy polymer.2

3.5 | Scanning electron microscopy

Field-emission gun scanning electron microscopy (FEG-SEM) was used to obtain high resolution images of the fracture surfaces of the tested single edge notched bending (SENB) specimens. A LEO Gemini 1525 microscope (Carl Zeiss, Germany) was used, with in-lens detection and an accelerating voltage of 5 kV. Samples from the cross-section were mounted on aluminium pin studs using a self-adhesive carbon sticker. To prevent charging effects, the samples were sputter coated with a 5–10 nm thick layer of chromium, using a Q150T S sputter coater (Quorum Technologies, UK). Silver paint was applied to electrically connect the sample surface to the pin stub.

4 | RESULTS AND DISCUSSION

4.1 | Introduction

Initial trials were conducted on bulk epoxy polymers modified with a hybrid carbon nanofiller, consisting of graphene nanoplatelets (GNPs) and multiwalled carbon nanotubes (MWCNTs) to determine the optimum mass ratio for good electrical conductivity. A mass ratio of 9:1 was selected, and the mechanical, thermal, electrical and fracture properties of hybrid-modified bulk epoxies were determined. The dispersion state and nanostructure of the hybrid nanofiller were described, and fractographic examination was performed to identify the toughening mechanisms. The experimentally-determined toughness values were compared to those theoretically predicted from analytical models using the identified toughening mechanisms.

4.2 | Selection of nanofiller

The optimum mass ratio between GNPs and CNTs in hybrid epoxy composites was examined by electrical impedance spectroscopy (EIS). Composites with a variable GNP:CNT ratio at a fixed nanofiller concentration of 0.5 wt% were fabricated by three-roll milling (3RM). Figure 1 shows the electrical conductivity versus alternating current (AC) frequency for the tested formulations. The conductivity increased by approximately three orders of magnitude at a frequency of 1 Hz (which will be the frequency at which conductivities are compared) when the GNP:CNT ratio is 9:1 compared to the GNP-only filled composite, see Figure 1. A further increase in
the CNT fraction to a mass ratio of 8:2 resulted in only a marginal increase of less than an order of magnitude in conductivity. Higher fractions of CNTs resulted in greater conductivities; with conductivity being proportional to the CNT fraction. The addition of higher CNT fractions is not desirable, as it results in higher blending viscosities, which impede processability. Rheological data was not obtained as this was outside the scope of this work, but there was a clear tendency for higher fractions of CNTs to result in more viscous blends. This is due to the stronger particle-particle and polymer-particle interactions in highly filled CNT-modified polymers as CNTs form a network readily compared to graphene sheets.31 Consequently, the ratio of GNP:CNT was set at 9:1, as this offered the best compromise between high electrical conductivity and low blending viscosity. Conductive epoxy matrices can be employed in a wide variety of applications such as lighting strike protection of fibrous composites,32 conductive coatings and electrostatic discharge protection; but at the same time a low enough viscosity is vital for the transfer of such matrices in fibrous composites using infusion-based processes.

4.3 | Tensile properties

The tensile properties of the GNP/CNT-modified epoxies are summarized in Figure 2. The Young’s modulus ($E_t$) of the unmodified epoxy was measured to be 2.9 GPa. Addition of the hybrid carbon nanofiller had no significant effect on the modulus, see Figure 2(a), despite the reported Young’s modulus of 1000 GPa for graphene.33 This is attributed to the weak interfacial adhesion between the matrix and carbon fillers. The presence of strong interfacial adhesion is necessary for effective reinforcement as it allows stress transfer from the high modulus filler to the low modulus polymer matrix.14 However, this can only be achieved when the two are chemically compatible. As both GNPs and CNTs were un-functionalized, the fillers have a graphitic non-polar surface, which is non-compatible with the polar epoxy matrix. No significant differences were observed in the tensile strength ($\sigma_t$) for the carbon-modified epoxies, see Figure 2(b). This agrees well with the earlier statement regarding the weak interfacial adhesion exhibited between the matrix and filler. Similarly, there is no significant effect of the filler content on the elongation to break for the carbon-modified epoxies, see Figure 2(c).

4.4 | Thermal properties

4.4.1 | Thermo-mechanical properties

The thermo-mechanical properties of the epoxy composites were examined using dynamic mechanical thermal analysis (DMTA), and Figure 3 shows the temperature dependence of storage modulus ($E'$) and loss factor (tan δ). Values of the glassy storage modulus ($E_{g}'$) at 35°C and rubbery storage modulus ($E_{r}'$) at 180°C, the glass transition temperature ($T_g$) and height of the tan δ peak are given in Table 1.

The storage modulus decreases with temperature increase due to the unstiffening of the epoxy matrix, see Figure 3(a).10,11 The $E_g'$ increased for all carbon-modified composites compared to the unmodified epoxy, but this increase is not proportional to filler loading and does not follow a clear trend. The increase in the $E_g'$ values is attributed to improved stiffness.10 The addition of the carbon nanofiller also has a positive influence on the $E_r'$, with a maximum increase of 182% compared to the unmodified epoxy being recorded for the 1 wt%-containing composite, see Table 1. In general, the value of $E_r'$ is associated with the degree of interaction between the polymeric matrix and filler, with higher $E_r'$ values indicating a stronger interaction. This stronger interaction is an outcome of the reinforcing effect of the hybrid nanofiller which leads to a restriction of the polymer chain mobility.10 The position of the tan δ peak corresponds to the glass transition temperature of the epoxy polymers and correlates to the cross-linking density of the polymeric chains. The incorporation of the carbon nanofiller does not produce a noticeable effect on the $T_g$, see Table 1, which implies that the filler does not affect the cross-linking...
density of the epoxy matrix. This is expected as both the GNP s and CNTs do not participate in the curing reaction between the resin and curing agent due to the absence of reactive functional groups. Nonetheless, the nanofiller has an obvious influence on the mobility of the polymeric chains, as viewed by the height of the tan $\delta$ peak, see Figure 3(b). The presence of nanofiller leads to a marked decrease in the height of the tan $\delta$ peak correlating directly to a reduction in the mobility of the polymer chains.

4.4.2 Thermal stability

The thermal stability of the epoxy polymers in nitrogen was investigated using thermogravimetric analysis (TGA), and Figure 4 shows the temperature dependence of mass loss and derivative mass loss. The temperatures where 5% ($T_{5\%}$) and 50% ($T_{50\%}$) mass losses have occurred, and where maximum thermal degradation ($T_{\text{max}}$) occurred, are given in Table 2. Values of the char yield ($Y_c$) are also listed, defined as the mass percentage of graphitic material remaining at 800°C.

The thermogram of the unmodified epoxy shows an identical behavior with those for the carbon-modified composites, see Figure 4(a), and is characterized by a two-step degradation process as described by Olowojoba et al. The addition of filler appears to have a negligible effect on the thermal stability of the resulting nanocomposites. This is evidenced by the static effect on the onset temperature of decomposition, defined as $T_{5\%}$, as well as on the temperature of maximum degradation,
max, see Table 2. Nevertheless, good improvements in the char yield are observed. The increase in $Y_c$ is not proportional to filler loading, with a maximum $Y_c$ of 16.9% recorded for the 0.01 wt%-containing material. This corresponds to an increment of 72% compared to the unmodified epoxy. The formation of higher char residues is due partly to the ability of graphene to promote carbonization on the polymer/filler interface, as well as to the intrinsically high heat resistance of the carbon nanofiller.35

4.5 | Electrical conductivity

The electrical conductivity of the epoxy polymers was determined using electrical impedance spectroscopy (EIS). Figure 5 shows a log–log plot of the electrical conductivity of the nanocomposites as a function of alternating current (AC) frequency. The samples containing 0.01 and 0.03 wt% of carbon nanofiller demonstrate a frequency-dependent increase in conductivity, similar to that of the unmodified epoxy matrix, which is typical behavior for dielectric, insulating materials. The sample containing 0.05 wt% of the hybrid nanofiller exhibits frequency-independent conductivity at frequencies below 1 Hz, followed by frequency-dependent behavior similar to that of the unmodified epoxy. With further increases in the filler content to 0.1 wt% and above, the conductivity becomes frequency independent, indicating a non-dielectric, conductive behavior, see Figure 5.

The conductivity of samples at a frequency of 1 Hz as a function of filler weight fraction is shown in Figure 6. There is a drastic increase in conductivity of about four orders of magnitude when the filler content increases

![Graphical representation of (a) storage modulus ($E'$) and (b) tan δ versus temperature for the GNP/CNT-modified epoxy composites with varying filler content [Color figure can be viewed at wileyonlinelibrary.com]](image)

**TABLE 1** Thermo-mechanical properties of the carbon-modified epoxy composites as determined by dynamic mechanical temperature analysis (DMTA)

| Filler concentration (wt%) | Storage modulus at 35°C ($E_0$) (GPa) | Storage modulus at 180°C ($E_r$) (MPa) | Glass transition temperature ($T_g$) (°C) | Maximum loss factor (tan δ max) |
|---------------------------|----------------------------------------|----------------------------------------|----------------------------------------|-------------------------------|
| 0                         | 2.64                                   | 11.7                                   | 158.7                                  | 1.53                          |
| 0.01                      | 2.88                                   | 13.1                                   | 157.5                                  | 1.23                          |
| 0.03                      | 2.81                                   | 11.7                                   | 159.1                                  | 1.31                          |
| 0.05                      | 2.70                                   | 14.9                                   | 160.5                                  | 1.26                          |
| 0.1                       | 2.75                                   | 14.0                                   | 159.6                                  | 1.29                          |
| 0.5                       | 2.80                                   | 14.2                                   | 157.4                                  | 1.24                          |
| 1                         | 2.69                                   | 33.0                                   | 158.6                                  | 1.16                          |
from 0.05 to 0.1 wt%. A further increase in conductivity to about $10^{-3}$ S/cm occurs when the filler loading is increased to 0.5 wt%. Further increases in the loading yield moderate improvements in conductivity, with a quadrupling of filler content from 0.5 to 2 wt% resulting in a mere increase of one order of magnitude in conductivity.

The significant and rapid increase in conductivity between 0.05 and 0.1 wt% indicates the formation of a percolated network by the GNP agglomerates and CNTs. This enables the electrical current to flow through the conductive nanocarbon fillers instead of through the insulating polymer matrix, resulting in this large increase in conductivity. The semi-log plot of conductivity versus filler content, see Figure 6, has the typical S-shape reported in the literature.22

According to percolation theory, the relationship between electrical conductivity ($\sigma$) and filler weight fraction ($p$) can be described by36:

$$\sigma = \sigma_0 (p - p_c)^t$$  \hspace{1cm} (2)

where $\sigma_0$ is the scaling factor, $p_c$ is the critical weight concentration (also known as the percolation threshold), and $t$ is a critical exponent which depends on the dimensionality of the system. Typically, values of $t$ between 1 and 1.3 reflect a two-dimensional (2D) system while those between 1.6 and 2 indicate a three-dimensional (3D) network.8,36

The data in the insert of Figure 6 is obtained by plotting $\log \sigma$ versus $\log (p - p_c)$ for random values of $p_c$ until the best linear fit is achieved. The line of best fit is
obtained for a $p_c$ value of 0.09 wt% with correlation coefficient ($R^2$) of 0.9998 and a gradient equal to the critical exponent ($t$) of 1.78. The obtained $t$ value indicates the carbon-modified composites exhibit a 3D conductive network, with charge flowing along the polymer matrix/filler interface as well as through the thickness of the stacked graphene agglomerates.

The percolation threshold, $p_c$ of 0.09 wt% is a significant improvement compared to $p_c$ values for conventional GNP-filled epoxy composites reported in the literature. A $p_c$ value of 1 wt% has been reported for composites prepared via milling/calendaring processes,23,24 while Han et al.20 and Monti et al.37 reported values of 1.0–1.2 wt% for composites manufactured via solution blending. Regarding the percolation threshold of single CNT-filled epoxies, this is significantly lower than those modified with GNPs, due to their unique 1D shape. Sandler et al.8 reported a $p_c$ value of 0.0025 wt% for MWCNT/epoxy composites. Consequently, the addition of even small fractions of CNTs can have a drastic effect on the percolation threshold of GNP-reinforced composites. In addition, the hybrid composites demonstrate a significantly improved bulk electrical conductivity compared to GNP/epoxy composites prepared via 3RM. For a loading of 1 wt% GNPs, Chandrasekaran et al.22 and Li et al.24 reported conductivities of about $10^{-5}$ and $10^{-9}$ S/cm, respectively. This demonstrates both the effectiveness of the fabrication process (i.e., 3RM), as well as the superiority of the hybrid nanofiller in producing composites with significantly enhanced electrical properties compared to conventional GNP-only filled systems. For comparison, the electrical conductivity for an epoxy composite modified with 1 wt% of MWCNTs is $10^{-2}$ S/cm,8 which is only an order of magnitude higher than what has been achieved in this work, for the corresponding loading. However, the MWCNT/epoxy composites will show a much higher blending viscosity than the hybrid composites which makes processing much more difficult.

### 4.6 Fracture toughness

The fracture toughness ($K_{IC}$) and fracture energy ($G_{IC}$) of the epoxy polymers were determined using single edge notched bending (SENB) tests. The effect of filler content on both $K_{IC}$ and $G_{IC}$ is shown in Figure 7. The addition of small fractions, between 0.01 and 0.1 wt%, of nanofiller leads to a small increment in the mean value of both $K_{IC}$ and $G_{IC}$. For higher filler contents, 0.5 and 1 wt%, $K_{IC}$ and $G_{IC}$ increase further; with a maximum value of 0.89 $\pm$ 0.03 MPa m$^{1/2}$ for $K_{IC}$ (corresponding to an average increase of 71% compared to the unmodified epoxy) and 240 $\pm$ 16 J/m$^2$ for $G_{IC}$ (average increase of 182% compared to the unmodified epoxy) for the 1 wt%-filled composite.

The obtained values are comparable to those reported in the literature for GNP/epoxy composites. Chandrasekaran et al.38 reported a $K_{IC}$ value of 0.81 $\pm$ 0.09 MPa m$^{1/2}$ for 1 wt% GNP-filled epoxy composite, representing a 43% increase compared to the unmodified
epoxy. Similarly, a $K_{IC}$ of $0.88 \pm 0.03$ MPa m$^{1/2}$ and a $G_{IC}$ of $222 \pm 20$ J/m$^2$, corresponding to a 47% and 131% increase, respectively, compared to the unmodified epoxy, were reported by Chong et al.$^{18}$ for an epoxy polymer modified with 1 wt% of GNPs. It is worth highlighting the potential of the hybrid nanofiller in toughening epoxies, by comparing its toughening effect against core shell rubber (CSR), a filler which has been shown to be very effective at toughening epoxies. For an epoxy polymer modified with 2 wt% of CSR, a noticeably lower $G_{IC}$ value of $154 \pm 22$ J/m$^2$ (corresponding to a mere 32% improvement compared to the unmodified epoxy) has been reported.$^1$

4.7 | Fractographic investigation

The fracture surfaces of the SENB specimens were examined using field emission gun scanning electron microscopy (FEG-SEM) following the conclusion of the tests, to investigate the quality of dispersion and identify the toughening mechanisms.

4.7.1 | Dispersion assessment

Images of the fracture surfaces at low magnifications were obtained to assess the quality of the dispersion of the nanofiller within the polymeric matrix, see Figure 8. The unmodified epoxy is a homogeneous polymer, see Figure 8(a). The characteristic river lines due to brittle fracture$^{34}$ can be disregarded for the purposes of considering the dispersion of the nanofiller. The graphene agglomerates appear as bright spots in the SEM images. (The magnification is too low to identify the dispersed CNTs). The GNP agglomerates are approximately 15 $\mu$m in diameter, see Figure 11(b), compared to a GNP platelet diameter of 4.5 $\mu$m (as listed by the manufacturer), indicating that these are composed of multiple GNPs. As can be seen in Figure 8, the adopted dispersion method (i.e., 3RM) produced a fairly uniform distribution of the nanofiller in the epoxy matrix. An increase in the filler content resulted in the appearance of a larger number of agglomerates and an increase in their size, although the quality of the dispersion remained unchanged as the loading of nanofiller increased.

4.7.2 | Fracture morphology

The fracture morphology of the tested SENB specimens is presented in Figure 9. The unmodified epoxy has a smooth fracture surface, see Figure 9(a), typical of a brittle, glassy polymer.$^{38}$ The characteristic river markings,$^{34}$ are caused by an excess of energy during brittle fracture of the epoxy polymer. This excess energy causes the crack to propagate on slightly different levels, leaving a step on the fracture surface which appears as a bright line in the electron micrographs. The local direction of crack propagation can be identified from the flow pattern of the river lines.$^{38}$

The incorporation of a minimal amount of nanofiller (i.e., 0.01 wt%) gives a significantly rougher fracture surface compared to the unmodified epoxy surface, see Figure 9(b). This is because the crack is deflected onto different height levels by the agglomerates.$^{38}$ The surface roughness increases gradually with increasing filler
content, as would be expected, as there are more agglomerates to deflect the crack. Closer examination revealed that only the GNPs resulted in crack deflection, and not the CNTs as these are too short. This was confirmed by the FEG-SEM images of pulled-out CNTs which did not show any river markings associated with crack deflection, see Figure 10, as well as from analytical modeling calculations (presented in Section 5).
The three dominant toughening mechanisms identified from the FEG-SEM images were: (a) CNT pull-out, (b) crack deflection by GNP agglomerates and (c) debonding of GNPs followed by pull-out. The presence of pulled-out CNTs is clearly evident in the electron micrographs, see Figure 10, due to their characteristic morphology which resembles that of spaghetti. A similar fracture morphology for an epoxy polymer
reinforced with CNTs has been reported, as well as for other type of CNT-reinforced matrices, such as polymer derived ceramics.

The interaction of the crack front with the GNP agglomerates can clearly be seen in Figure 11(a). As outlined earlier, the crack front is deflected when it meets the GNP stacks, resulting in a height difference between the original crack front and the deflected crack front. This difference in height results in a step on the fracture surface which causes the river markings, as shown in Figure 11(b). The river markings originate from the GNP particles (indicated by red circles), resulting in a characteristic tail-like feature parallel to the crack growth direction, as shown in Figure 9. The overall outcome is for the crack to take a more tortuous path, accounting for the rough surface morphology, see Figure 9(b-g). The absence of characteristic river lines around the pulled-out CNTs, see Figure 10, is a clear indication that the CNTs do not cause crack deflection.

The debonding of GNP particles from the epoxy matrix followed by pull-out is indicated by the red arrows in Figure 12. This results in the detached sheets appearing as particles that have pulled out in the opposite fracture surfaces, similar to the particle shown in Figure 11(b). The debonding and pull-out of GNPs are two well-established toughening mechanisms in GNP-reinforced epoxies, and are clearly identifiable in agglomerates that are perpendicularly oriented to the direction of crack propagation.

5 | MODELING STUDIES

5.1 | CNT contribution

The fracture energy of the epoxy composites reinforced with the hybrid nanofiller was predicted using analytical models to calculate the toughening contributions of the individual mechanisms. For CNT reinforcement, pull-out of CNTs was clearly seen, see Figure 10, which implies that debonding must have occurred. The voids created by debonding reduce the constraint on the epoxy, allowing the matrix to undergo plastic void growth. Additionally, long CNTs will rupture following their pull-out from the matrix. The toughening contribution from the CNTs, $\psi_{\text{CNT}}$, can be described by:

$$\psi_{\text{CNT}} = \Delta G_{\text{po(CNT)}} + \Delta G_{\text{db(CNT)}} + \Delta G_{\text{v(CNT)}} + \Delta G_{\text{r(CNT)}}$$

where $\Delta G_{\text{po(CNT)}}$ is the energy contribution from the CNT pull-out, $\Delta G_{\text{db(CNT)}}$ is the energy contribution from interfacial debonding, $\Delta G_{\text{v(CNT)}}$ is the energy contribution from plastic void growth and $\Delta G_{\text{r(CNT)}}$ is the energy contribution due to the elastic deformation of the CNTs prior to rupturing.

The energy contribution due to CNT pull-out can be described by:

$$\Delta G_{\text{po}} = \frac{V_{\text{fpo}} l_e^2 \tau_i}{3 r_f}$$

where $V_{\text{fpo}}$ is the volume fraction of nanotubes which are observed to pull-out, $l_e$ is the effective pull-out length, $\tau_i$ is the interfacial shear strength and $r_f$ is the radius of the nanotube. The effective pull-out length, $l_e$, was determined from the FEG-SEM images to be equal to 0.17 μm. Ladani et al. argued that the longest possible pull-out length of CNTs is equal to half the critical length ($l_{fc}$), which is given by:

$$l_{fc} = \frac{\sigma_f d_f}{2 \tau_i}$$

FIGURE 10 FEG-SEM images of fractured surfaces of GNP/CNT-modified epoxy composites, showing CNT pull-out. Pulled out CNTs are indicated by red circles [Color figure can be viewed at wileyonlinelibrary.com]
where $\sigma_t$ is the CNT tensile strength and $d_f$ is the diameter of the nanotube. The critical length, $l_c$, is equal to 0.88 $\mu$m, which translates to a longest possible pull-out length of 0.44 $\mu$m. This means that the effective pull-out length, $l_e$, of 0.17 $\mu$m is about 40% of the longest possible pull-out length.

Interfacial debonding enables the nanotubes to be pulled-out from the matrix, and the epoxy matrix to plastically deform via void growth. The interfacial debonding energy, $\Delta G_{db}$, is described by:

$$\Delta G_{db} = \frac{V_{fdb} l_f G_i}{d_f}$$  (6)

where $V_{fdb}$ is the volume fraction of nanotubes which debond, $l_f$ is the length of the nanotube, and $G_i$ is the interfacial fracture energy between the CNTs and the epoxy.

The fracture energy contribution from the plastic void growth of the epoxy matrix is described by:

$$\Delta G_v = \left(1 - \frac{\mu_m^2}{3}\right) \left(V_{fV} - V_{fP}\right) \sigma_{yc} r_{yu} K_{vm}^2$$  (7)

where $V_{fV}$ and $V_{fP}$ are respectively the volume fraction of the voids and volume fraction of nanotubes which exhibit void growth around them, and $\mu_m$ is a material constant allowing for the pressure dependency of the yield stress. $K_{vm}$ is the maximum stress concentration for the von Mises stresses around a debonded CNT, and lies between 2.11 and 2.12. $\sigma_{yc}$ is the compressive yield stress of the unmodified epoxy, and $r_{yu}$ is the Irwin plastic zone size at fracture of the unmodified epoxy, which can be calculated using:

$$r_{yu} = \frac{1}{6\pi} \frac{E_i G_{CV}}{(1-\nu^2)\sigma_{yt}^2}$$  (8)

where $G_{CV}$ and $\sigma_{yt}$ is the fracture energy and tensile yield stress of the unmodified epoxy, respectively and $\nu$ is the Poisson’s ratio of the epoxy polymer. By using Equation (8),

**FIGURE 11** FEG-SEM images of fractured surfaces of GNP/CNT-modified epoxy composites, showing: (a) crack deflection around graphene agglomerates (agglomerates are indicated by red circles) and (b) close-up of a graphene agglomerate where the crack front has deflected leaving behind the characteristic tail-like feature (direction of crack propagation indicated by a dotted arrow) [Color figure can be viewed at wileyonlinelibrary.com]

**FIGURE 12** FEG-SEM images of fractured surfaces of GNP/CNT-modified epoxy composites, illustrating GNP sheet detachment due to debonding. The red arrows indicate the area where detachment has occurred, with the direction of crack propagation indicated by dotted arrows [Color figure can be viewed at wileyonlinelibrary.com]
the Irwin plastic zone size of the epoxy, \( r_{\nu m} \), at the crack tip is calculated to be 3.14 \( \mu m \). The average length of the nanotubes, \( l_p \), is only 1.5 \( \mu m \), and as has been argued by Johnsen et al.\(^40\) they are unlikely to cause crack deflection as the obstacle dimension is smaller than that of the plastic zone. This was confirmed by fractographic investigation, where river lines associated with crack deflection were not seen for the CNTs, see Figure 10.

Each void is assumed to be a truncated cone with the smaller diameter equal to the diameter of the nanotube (\( d_f \)) and the larger diameter is the void size \( d_v \), where \( \gamma_f \) is the compressive fracture strain of the unmodified epoxy. In the proposed model, it is assumed that all nanotubes debond, pull-out and show plastic void growth; hence, \( V_f = V_{ fp0} - V_{ db} = V_{ fp} \). In Equation (7), the subtraction of \( (V_f - V_{ fp}) \) becomes \( (V_{ fp} - V_f) \). Considering that the number of nanotubes per unit area, \( N \), can be expressed as \( V_f = N \pi r_f^2 \), and that the radius of a void, \( r_v \), equals \( (1 + \gamma_f) r_f \), \( V_f - V_f \) can be written as:

\[
V_f - V_f = N \pi \left(1 + \gamma_f\right)^2 \frac{r_f^2}{2} - N \pi r_f^2 = V_f \left(1 + \gamma_f\right)^2 - 1
\]

Based on Equation (9) for a CNT weight fraction of 0.1 wt%, \( V_f - V_f = 0.18 \). This is in excellent agreement with the corresponding value of 0.22 reported by Ladani et al.\(^41\) which the authors experimentally determined from the fracture surfaces.

The energy contribution due to the elastic deformation of the CNTs prior to rupturing is described by\(^41\):

\[
\Delta G_e = \frac{V_{fp0} \sigma_f^2 l_f}{2 E_f}
\]

where \( E_f \) is the Young’s modulus of the CNTs.

The predicted values of the fracture energy for the different toughening mechanisms, due to CNT reinforcement alone, are presented in Table 3. The major toughening mechanisms are debonding and void growth, each contributing about 2.6 J/m\(^2\) at the highest weight fraction (i.e., 0.1 wt%). The contribution from CNT pull-out and CNT rupture is negligible, being less than 0.21 J/m\(^2\). As will be seen later, the overall toughening contribution from CNTs is very small compared to that of GNPs.

5.2 GNP contribution

For GNP reinforcement, crack deflection was clearly seen from the FEG-SEM images, see Figure 11, in addition to particle/matrix debonding followed by pull-out, see Figure 12. As the debonding and pull-out mechanisms take place, the voids formed may increase in size by deformation of the epoxy matrix through plastic void growth as described elsewhere.\(^2,40\) The energy contribution from the elastic deformation of GNPs up to their rupture is an additional factor that has to be taken into consideration.\(^21\) The toughening contribution provided by the presence of GNPs, \( \psi_{GNP} \), in the epoxy matrix can be summed by:

\[
\psi_{GNP} = \Delta G_{po(GNP)} + \Delta G_{db(GNP)} + \Delta G_{v(GNP)} + \Delta G_{r(GNP)} + \Delta G_{cd}
\]

where \( \Delta G_{po(GNP)} \) is the energy contribution from GNP pull-out, \( \Delta G_{db(GNP)} \) is the energy contribution from GNP debonding, \( \Delta G_{v(GNP)} \) is the energy contribution from plastic void growth around debonded GNPs, \( \Delta G_{r(GNP)} \) is the energy contribution from the elastic deformation of GNPs prior to rupturing and \( \Delta G_{cd} \) is the energy contribution from crack deflection.

The energy dissipated by the pull-out of 2D platelets such as GNPs can be calculated according to\(^21\):

\[
\Delta G_{po} = \frac{2 V_f t_p l_{po}^2}{t_p}
\]

where \( t_p \) is the platelet thickness, \( l_{po} \) is the length of the platelet that gets pulled-out of the matrix and \( \tau_i \) is the interfacial shear strength between the GNP and the epoxy. The GNP pull-out length, \( l_{po} \), is virtually impossible to determine with any high degree of accuracy from the FEG-SEM images of the fracture surfaces. Ladani et al.\(^21\) argued that the longest pull-out length is equal to half the critical length of the GNPs embedded in the matrix, with the critical platelet length, \( l_{pc} \) described by\(^21\):

\[
l_{pc} = \frac{\sigma_G t_p}{\tau_i}
\]

where \( \sigma_G \) is the tensile strength of the GNP. Equation (13) produces a critical platelet length, \( l_{pc} \) of 2.02 \( \mu m \); hence the platelet pull-out length, \( l_{po} \) equals 1.01 \( \mu m \).

The rupture energy is associated with the elastic deformation of GNPs up to their tensile failure point, which is given by\(^21\):

\[
\Delta G_r = \frac{V_f L_p \sigma_G^2}{2 E_G}
\]

where \( L_p \) is the lateral size of the platelet and \( E_G \) is the Young’s modulus of the GNPs.
Prior to the pull-out and rupture processes, the GNPs debond from the epoxy matrix. The energy due to interfacial debonding is given by

$$\Delta G_{db} = \frac{2V_f l_{po} G_i}{t_p}$$  \hspace{1cm} (15)$$

where $G_i$ is the interfacial fracture energy between the GNP and the epoxy.

Plastic void growth of the matrix is initiated by the debonding of the GNPs from the epoxy, and the fracture energy contribution can be calculated by

$$\Delta G_v = \left(1 - \frac{r_m^2}{3} \right) (V_{fo} - V_f) \sigma_{yc} r_{yu} K_{sm}^2$$  \hspace{1cm} (16)$$

where $V_{fo}$ and $V_f$ are respectively the volume fraction of the voids and volume fraction of GNPs. The void growth model assumes that all GNPs show void growth around them, and that the platelets are square, with each side equal to the lateral size. The voids will grow to a final lateral size of $L_v = (1 + \gamma_f)L_p$ and a thickness of $t_v = (1 + \gamma_f) t_p$. Considering that the total number of GNPs per unit area is given by $N$, which is related to the volume fraction ($V_p$) by: $V_p = N L_p t_p$, the subtraction of $(V_{fo} - V_f)$ can be written as:

$$V_{fo} - V_f = N \left(1 + \gamma_f \right) L_p \left(1 + \gamma_f \right)$$

$$t_p - N L_p t_p = V_f \left[ (1 + \gamma_f)^2 - 1 \right]$$  \hspace{1cm} (17)$$

The energy contribution from crack deflection, $\Delta G_{cd}$, was derived by Faber and Evans. The analysis was based on the initial tilt and the maximum twist for disc-shaped particles. The Irwin plastic zone of the unmodified epoxy, $r_{yu}$, was calculated as 3.14 $\mu$m (using Equation 8). Considering that the average GNP length, $L_p$, is 3.9 $\mu$m, crack deflection is expected to be a significant toughening mechanism, as seen from the fracture surfaces, see Figure 11.

The predicted fracture energy for the toughening contributions of the GNPs are presented in Table 4. The most dominant mechanism is crack deflection, which contributes significantly even at very low weight fractions. For a weight fraction of 0.009 wt% the model predicts an increase in fracture energy of about 17 J/m$^2$, when all other four mechanisms have a negligible effect at that loading. Nevertheless, the toughening contributions from platelet pull-out, debonding and void growth does become significant at higher weight fractions. Similarly to the CNTs, the contribution from GNP rupture is insignificant.
Comparing the toughening contributions for CNT and GNP reinforcement in Tables 3 and 4, it is evident that the toughening in the hybrid nanocarbon composites comes entirely from the GNPs. This is for two reasons: (a) the GNP concentration in the matrix is nine times that of CNTs, and (b) crack deflection was seen to be the dominant toughening mechanism. Hence the inability of the CNTs to cause the crack front to deflect makes them a considerably poorer toughening reinforcement compared to GNPs.

The parameters used in this modeling study for predicting the toughening contributions of CNTs and GNPs, are given in Table 5.

| Name                        | Symbol | Unit | Value | Source      |
|-----------------------------|--------|------|-------|-------------|
| CNT length                  | \(l_f\) | \(\mu m\) | 1.5   | Present study |
| CNT diameter                | \(d_f\) | nm   | 9.5   | Present study |
| Density of CNT              | \(\rho_f\) | g/cm\(^3\) | 1.74 | 44 |
| Young's modulus of CNT      | \(E_f\) | GPa  | 180   | 45 |
| GNP length                  | \(L_p\) | \(\mu m\) | 3.9   | Present study |
| GNP thickness               | \(t_p\) | nm   | 19    | Present study |
| Density of GNP              | \(\rho_p\) | g/cm\(^3\) | 2.2   | 21 |
| Young's modulus of GNP      | \(E_G\) | GPa  | 1000  | 33 |
| Young's modulus of unmodified epoxy | \(E_t\) | GPa  | 2.9   | |
| Density of unmodified epoxy | \(\rho_m\) | g/cm\(^3\) | 1.15  | Present study |
| Fracture energy of unmodified epoxy | \(G_{CU}\) | J/m\(^2\) | 85.3  | Present study |
| Effective pull-out length of CNT | \(l_e\) | \(\mu m\) | 0.17  | Present study |
| Interfacial shear strength  | \(\tau_i\) | MPa  | 47    | 6,18,46 |
| Poisson's ratio of unmodified epoxy | \(\nu\) | —    | 0.35  | 2 |
| Compressive yield stress of unmodified epoxy | \(\sigma_{yc}\) | MPa  | 107   | 18 |
| Tensile yield stress of unmodified epoxy | \(\sigma_{yt}\) | MPa  | 69    | |
| Compressive fracture strain of unmodified epoxy | \(\gamma_f\) | —    | 0.91  | 18 |
| Pressure-dependent yield stress parameter | \(\mu_{m}\) | —    | 0.2   | 42 |
| Maximum von Mises stress concentration | \(K_{vm}\) | —    | 2.11  | 2 |
| Interfacial fracture energy  | \(G_i\) | J/m\(^2\) | 25    | 6,18,47 |
| Tensile strength of CNT      | \(\sigma_f\) | GPa  | 8.7   | 41 |
| Tensile strength of GNP      | \(\sigma_G\) | GPa  | 5     | 21 |

5.3 Combined toughening effect

The combined toughening contribution from CNTs and GNPs is plotted against the nanocarbon content in Figure 13. There is excellent agreement between the experimental and theoretically predicted values of the fracture energy. The model slightly overestimates the fracture energy at the highest loading (i.e., 1 wt%). This is partly owed to the fact that the predicted energy contribution for GNP pull-out and void growth doubles in the loading range between 0.5 and 1 wt%, see Table 4, while
at the same time the experimental values appear to flatten out beyond 0.5 wt%.

6 | CONCLUSIONS

An epoxy polymer was modified with a hybrid filler comprising of GNPs and CNTs. A mass ratio of 9:1 was selected as this offered the best compromise between high electrical conductivity and low blending viscosity.

The hybrid nanofiller did not affect the tensile properties and glass transition temperature of the epoxy polymer, due to the relatively poor interfacial adhesion. This is attributed to the absence of functional groups in the surface of the nanofillers which prohibits the formation of covalent bonding between matrix and filler, and does not allow favorable molecular interaction. However, the incorporation of the nanofiller has a positive influence in the improvement of both electrical conductivity and fracture toughness. With the addition of 1 wt% nanofiller, the electrical conductivity increased by more than eight orders of magnitude compared to the unmodified epoxy. A maximum fracture energy of 240 J/m² was recorded for the same filler loading, representing an increase of 182% in comparison to the pristine epoxy. Percolation theory showed that the hybrid nanofiller results in an electrical percolation threshold of 0.09 wt%, which is more than 10 times lower than that of conventional GNP/epoxy composites. This is attributed to the high aspect ratio of the CNTs which have the ability to bridge the GNP agglomerates resulting in shorter conduction pathways.

Investigation of the fractographic surfaces, showed that the dominant toughening mechanism was crack deflection by the GNPs. The fracture energy of the carbon modified composites was predicted using simple analytical models, and there was excellent agreement with the experimentally determined values. The modeling studies confirmed that the GNP crack deflection mechanism made the greatest contribution. Additionally, it was concluded that the toughening contribution from the CNTs is insignificant when compared to that of the GNPs. Overall, the CNTs contribute to the good electrical conductivity of the composites, while the GNPs contribute to the improved toughness. Such modified epoxy matrices can be of particular usefulness in the development of conductive adhesives and functional multiscale composites; for instance, lightning strike damage tolerant fiber reinforced composites, such as those employed in wind turbines and aircraft exterior structures.

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