

Multifunctional Properties of Epoxy Nanocomposites Reinforced by Aligned Nanoscale Carbon

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Abstract

The present paper compares improvements to the fracture energy and electrical conductivity of epoxy nanocomposite materials reinforced by one-dimensional carbon nanofibres (CNFs) or two-dimensional graphene nanoplatelets (GNPs). The effects of the shape, orientation and concentration (i.e. 0.5, 1.0, 1.5 and 2.0 wt%) of nanoscale carbon reinforcements on the property improvements are presented. Alignment of the nano-reinforcements in the epoxy nanocomposites is achieved through the application of an alternating current (AC) electric-field before gelation and curing of the epoxy resin. Alignment of the nano-reinforcements increased the electrical conductivity and simultaneously lowered the percolation threshold necessary to form a conductive network in the nanocomposites. Nano-reinforcement alignment also increased greatly the fracture energy of the epoxy due to a higher fraction of the nano-reinforcement participating in multiple intrinsic (e.g. interfacial debonding and void growth) and extrinsic (e.g. pull-out and bridging) toughening mechanisms. A mechanistic model is presented to quantify the contributions from the different toughening mechanisms induced by CNF and GNP nano-reinforcements on the large improvements in fracture toughness. The model results show that one-dimensional CNFs are more effective than GNPs at increasing the intrinsic toughness of epoxy via void growth, whereas two-dimensional GNPs are more effective than CNFs at improving the extrinsic toughness via crack bridging and pull-out.

Keywords: Nanocomposite, Electrical conductivity, Fracture toughness, Modelling,

1. Introduction

Thermosetting polymers, such as epoxies, are used in a wide range of fibre reinforced composite and coating applications. Despite having many desirable properties, unmodified epoxies typically have low toughness and electrical conductivity. Nanoscale carbon-based reinforcements, such as graphene nanoplatelets (GNPs) [1–3], carbon nanotubes (CNTs) [4–6] and carbon nanofibres (CNFs) [7–10], have been used to increase the

toughness and electrical conductivity of commercial epoxies. In addition, carbon-based nano-reinforcements increase the matrix-dominated properties of fibre-reinforced polymer composites, such as the inter- and intra-ply mechanical properties and the electrical conductivity [11–14]. The extent of the property improvements depends on the morphology (e.g. CNFs and CNTs are one-dimensional while GNPs are two-dimensional), volume content and orientation of the carbon nano-reinforcements. In particular, improvements to many important properties of epoxy nanocomposites containing randomly-oriented carbon nano-reinforcements are often significantly lower than what might be achieved were the nano-reinforcements aligned in the optimum direction [15–17]. Goh et. al. [18] recently reported a thorough review of the literature highlighting various *ex-situ* and *in-situ* techniques for aligning carbon nano-reinforcements in polymer matrices and their influence on electrical and mechanical properties. *Ex-situ* alignment techniques such as electrospinning [19] and grafting of radially-aligned CNTs onto micro-scale fibres [20] have shown great potential for improving mechanical properties of polymer composites. Similarly, electric- [2,10] and magnetic-fields [7] have recently been employed with great success to *in-situ* align carbon nano-reinforcements in thermosetting polymers, while the polymers were in the liquid ('monomeric') phase prior to cure. In the presence of an electric-field between a pair of parallel electrodes, the nano-reinforcement may align to form a chain-like structure in the direction of the external field, which may be easily manipulated and oriented in any desired direction [21]. The resultant nanocomposites containing aligned carbon nano-reinforcements often outperform their randomly-orientated counterparts [2,10,16].

Research into polymer nanocomposites has recently advanced to a level where several important properties, such as strength and stiffness, can be predicted using various modelling approaches [17,19]. This enables an effective 'materials design' approach to be adopted for this new class of materials, which reduces the cost and accelerates the introduction of novel and improved nanocomposite materials. However, only limited research has been reported on the comprehensive modelling of the fracture properties of nanocomposites [10,22,23], and these studies have focused on one-dimensional nano-reinforcements such as CNTs and CNFs. Thus, in spite of recent efforts, there is a lack of suitable fracture models that enable the optimum design of nanocomposites with two-dimensional nano-reinforcements for high crack resistance.

We aim to identify the effects of shape, orientation and concentration of the nano-reinforcements on the electrical conductivity and fracture toughness of epoxy nanocomposites. Firstly, the alignment of CNFs and GNPs in liquid epoxy using an external alternating current (AC) electric-field is investigated, and the electro-mechanical mechanisms controlling the rotation and subsequent alignment of the carbon nano-reinforcements and its effects on the electrical conductivity are studied. Secondly, the improvements to the fracture toughness resulting from addition of various concentrations of the carbon nano-reinforcements (both aligned and randomly-oriented) in the epoxy are measured and compared. A mechanistic fracture model is presented to quantify the improvements in fracture toughness of polymer nanocomposites by one-

dimensional CNFs or two-dimensional GNPs. Finally, the numerical accuracy of the model and its sensitivity to input parameters are compared against experimental toughness values for the epoxy polymer containing CNFs or GNPs.

2. Materials and Experimental Methodology

The carbon nano-reinforcements used in this study were commercially available carbon nanofibres (Pyrograf® - III, grade PR-24-XT-HHT supplied by Applied Sciences Inc.) and graphene nanoplatelets (xGnP, M grade supplied by XG Science). The CNFs had a diameter of about 70-200 nm and a length of 50-200 µm, while the GNPs had a thickness ranging from 1 to 20 nm and platelet diameter of ~1-50 µm. The GNPs had an average thickness of ~8 nm which equates to about 18 graphene sheets stacked together to form each platelets based on the d-spacing of 0.34 nm [2]. The epoxy resin used was a liquid blend of about 60-100% of bisphenol A and 10-30% of bisphenol F [24] ('R105' from West System) while the curing agent ('206' from West System) was a blend of aliphatic amines and aliphatic amine adducts based on diethylenetriamine and triethylenetetramine. The ratio of resin to hardener used for the epoxy system was 5:1 by weight. Carbon-fibre reinforced-plastic (CFRP) laminate substrates (150 x 250 x 2.65 mm) were made using 12 plies of unidirectional T700 carbon-fibre/epoxy prepreg (VTM 264 supplied by Applied Composites Group).

Epoxy nanocomposites with contents of 0.5, 1.0, 1.5, and 2.0 wt% of GNPs were fabricated by combining sonication and calendaring processes. Epoxy nanocomposites with exact same CNF weight content were prepared by using only the calendaring process. The GNPs was first mixed with the liquid epoxy resin using a Hielscher UP200S ultrasonic homogenizer (operated at 0.5 cycles and 50% amplitude) for 30 minutes, which broke-up the graphene agglomerates. The mixture was then further processed by a three-roll mill calendaring (Dermamill 100) ten times at 300 rpm with a roller-gap distance of 20 µm. Similarly, the CNFs with desired weight content were first mixed with dispersion-aiding additives based upon solvent-free acrylate copolymers, namely Disperbyk-191 and -192 (supplied by BYK®). The dispersive surfactants that were added to the CNFs were equal to the weight of CNFs, resulting in a mixture of CNFs:D-191:D-192 at weight ratio of 1:1:1. The CNF-surfactant mixture was then added to epoxy resin and hand mixed for 5 min. This mixture was then passed four times through the three-roll mill at 150 rpm with progressively smaller gap size until the smallest gap setting of 20 µm had been reached. The CNF/epoxy mixture was processed at a lower calendaring speed in order to avoid the excessive shear rate experienced by the CNFs during dispersion. High calendaring shear rate has been reported to reduce the length of CNFs [25] and CNTs [26] resulting in lower conductivity and fracture toughness of the epoxy nanocomposites.

As shown in **Fig. 1**, double cantilever beam (DCB) joints were prepared using the epoxy nanocomposite as a 2 mm thick adhesive layer bonding the two CFRP laminate substrates. The curing agent

was added to the dispersed nano-reinforcement/epoxy resin mixture and hand-mixed for approximately 5 minutes. The mixture was then degased and poured between the substrates to form the DCB joints. The substrates also acted as the electrodes for the application of the AC electric-field in the through-thickness direction. In the present work, DCB joints were prepared using the epoxy nanocomposite as the adhesive layer with four concentrations (i.e. 0.5, 1.0, 1.5 and 2.0 wt%) of CNFs or GNPs, and with two different orientations (i.e. randomly-oriented and aligned) of the CNFs or GNPs. An AC electric field of 30 V/mm at 10 kHz was applied during the initial one hour period of the resin cure cycle, in order to align the nano-reinforcements in the through-thickness direction of the epoxy nanocomposite layer before resin gelation which occurred within 1 hour at 25 °C [27]. The electric field induced alignment of the nano-reinforcement ceased once the resin began to gel. The nanocomposite adhesive layer was cured to its working strength at room temperature (i.e. 25 °C) for 48 hours in accordance with the resin supplier's recommendations. Additional details of the general procedure for testing and analysis of the DCB composite joints, in accordance with the ISO 25217 [28], were reported in our previous work [2,10].

In order to study the electrical conductivity of the epoxy nanocomposites, the nano-reinforcement /epoxy mixtures were placed in a silicon rubber mould. The mould was then placed between two aluminium plates which were used to apply an AC electric-field of strength 30 V/mm in the thickness direction during the initial one hour period (resin gelation time) of the curing cycle of the epoxy resin. The epoxy was cured at room temperature for 48 hours and then machined into rectangular test specimens of size $25 \times 20 \times 2$ mm for electrical conductivity measurements following the ASTM D257 standard. The DC conductivity measurements were performed using a high resistance meter (Agilent 4339B) at room temperature. Similarly, the AC conductivity measurements were also performed at room temperature using an impedance analyser (HP4192A).

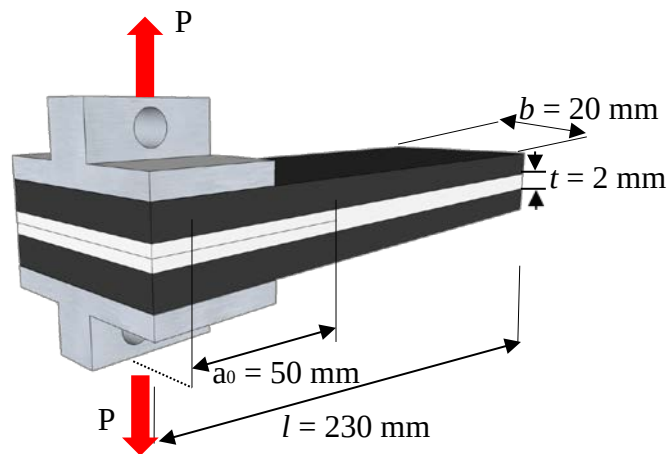


Fig 1. Schematic diagram of the double cantilever beam (DCB) specimen for fracture toughness testing

3. Results and Discussion

3.1 Electric-field induced alignment of the nano-reinforcements

1 The electric-field induced alignment of the CNFs was investigated using transmission electron microscopy
2 (TEM) of 90 nm thick slices of the epoxy nanocomposites. The materials with random or aligned nano-
3 reinforcements were sectioned using ultramicrotomy in the through-thickness direction, and typical TEM
4 images are shown in **Fig. 2a₁** and **a₂**. As expected, without the application of an electric field the CNFs were
5 randomly oriented in the nanocomposites. Using the electric field, the CNFs aligned (**Fig. 2a₂**) in the
6 direction parallel to the external field. Similarly, scanning electron microscopy (SEM) examination of
7 cryogenically fractured GNP-epoxy nanocomposites revealed alignment of the GNPs in the direction along
8 the externally applied electric-field (**Fig. 2b₂**). The degree and rate of alignment was not significantly
9 different between the one-dimensional (CNFs) and two-dimensional (GNPs) nano-reinforcements for the
10 electric-field conditions used in the present study.

11

12

13 **Fig 2.** TEM images of the epoxy nanocomposites: (a₁) 1.0 wt% of CNFs and randomly-oriented and (a₂) 1.0
14 wt% of CNFs and aligned via the application of the AC electric-field. SEM images of epoxy
15 nanocomposites: (b₁) 1.0 wt% GNPs and randomly-oriented and (b₂) 1.0 wt% aligned GNPs via the
16 application of the AC electric-field. The arrows on the micrographs indicate the orientation of the nanoscale
17 reinforcements. The direction of the applied AC electric-field is indicated by the arrow at the top right-hand
18 corner in (a₂) and (b₂).

19

20 Alignment of the nano-reinforcements in the direction of the externally applied electric field can be
21 explained from the process of dielectrophoresis. Namely, in the presence of the external electric field, the
22 nano-reinforcements immersed in the epoxy (which is a dielectric medium) gain a dipole moment from their

polarization, which results from the differences in the electrical conductivity and dielectric properties between the carbon nanoparticles and the liquid epoxy. For CNFs and GNPs, due to their shape anisotropy, the longitudinal polarizability is at least an order of magnitude greater than the transverse polarizability [2,29]. Therefore, the interaction between the applied electric field and the induced dipole on the CNFs and GNPs generates a torque causing both types of nano-reinforcement to rotate and align in the liquid resin. Upon gelation and subsequent curing of the resin, the aligned nano-reinforcements remain in place in the resulting epoxy nanocomposite.

3.2 Electrical Conductivity

Fig. 3 shows the electrical conductivity of the CNF- and GNP-epoxy nanocomposites as a function of the frequency, using logarithmic scales. For the nanocomposites containing aligned nano-reinforcements, measurements were made parallel to the alignment direction (i.e. through-thickness direction of the DCB joint). For the randomly-oriented GNP-epoxy nanocomposites with loadings of 0.5 wt% and 1.0 wt% (**Fig. 3b**) there is an increase in the capacitive component with increasing frequency, which is similar to that measured for the unmodified epoxy. However, for the 0.5 wt% aligned GNP-epoxy nanocomposite, there is a frequency-independent conductivity response at frequencies below about 100 Hz, and at higher frequencies the response is similar to that of the unmodified epoxy. A similar trend also occurs for the 0.5 wt% randomly-orientated CNF-epoxy nanocomposite with a transition in frequency dependency at about 10 kHz (see **Fig. 3a**).

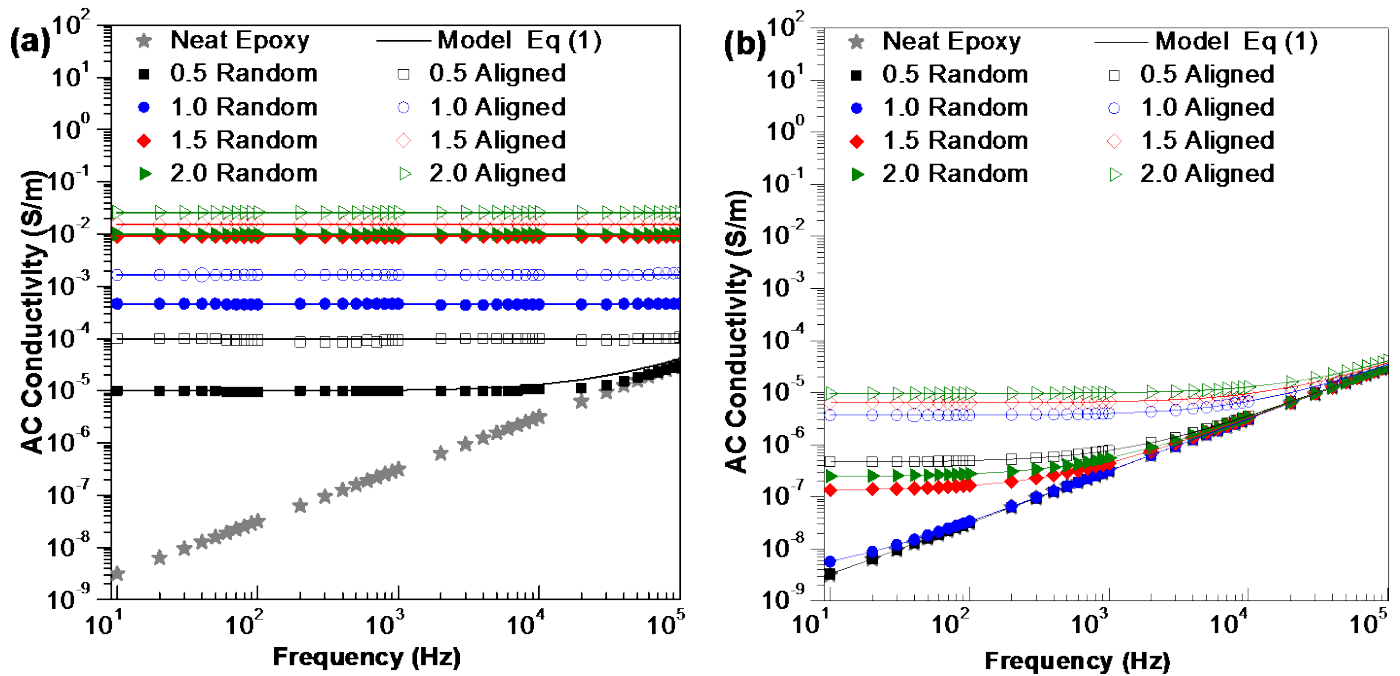


Fig 3. Electrical conductivity of the epoxy nanocomposites as a function of frequency. AC conductivity of the (a) CNF-epoxy polymer nanocomposites and (b) GNP-epoxy polymer nanocomposites; all the solid lines indicate the best fit using Equation (1).

The frequency-dependent results of the electrical conductivity can be correlated using the universal dielectric relationship originally reported by Jonsher [30,31] for a wide range of dielectric materials,

$$\sigma(\omega) = \sigma_{dc} + A\epsilon_0\omega \quad (1)$$

where σ_{dc} is the DC conductivity, ϵ_0 is the dielectric permittivity of the free space ($\epsilon_0 = 8.845 \times 10^{-12} \text{ F/m}$), ω is the angular frequency, and A is a constant. This conductivity relationship is applicable for frequencies below 1-10 GHz [30]. For a nanocomposite containing a conductive filler (e.g. CNFs, GNPs), the conductivity is governed by percolation paths at low frequency and the dielectric matrix at high frequency. By curve-fitting the AC conductivity results of the unmodified epoxy, the value of the parameter A has been found to be 5.65. It is interesting to note that the same value of A can be used to model the frequency-dependent conductivity of all the concentrations of CNFs and GNPs used in the epoxy nanocomposites in the present investigation. The appearance of a DC plateau for the 0.5 wt% aligned GNP-epoxy nanocomposite and the 0.5 wt% random CNF-epoxy nanocomposite indicates a transition from the insulating regime dominated by the epoxy to a conducting regime, which reflects the formation of some percolating nano-reinforcement networks. At higher concentrations of nano-reinforcements in the epoxy, the AC conductivity is dominated by the DC conductivity and becomes frequency-independent for both the CNF- and GNP-epoxy nanocomposites, irrespective of their orientation in the epoxy.

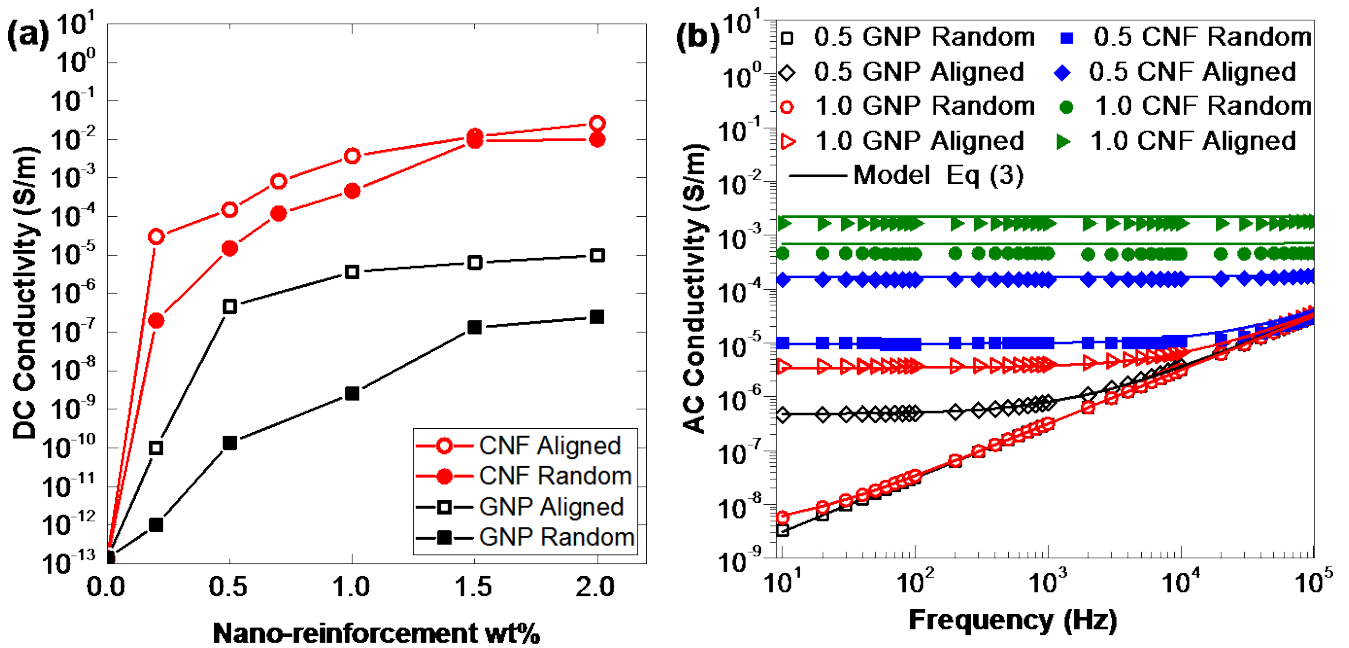


Fig 4. (a) Effect of concentration and alignment of CNFs and GNPs on the DC electrical conductivities of the epoxy nanocomposites; (b) comparison of the AC electrical conductivity results with the model given by Eq. (3) which is represented by the solid lines for corresponding concentrations of nano-reinforcement.

The effects of nano-reinforcement content and orientation on the DC electrical conductivity of the epoxy nanocomposites is shown in **Fig. 4**. The electrical conductivity of the randomly-oriented and aligned nanocomposites increase with the nano-reinforcement concentration up to ~1.5wt%, above which there is little or no further increase. The electrical conductivity does not increase further due to the difficulty in achieving a homogeneous dispersion at relatively high concentrations of nano-reinforcement using the

calendering process, but instead there occurs a significant agglomeration and clustering of the nano-reinforcement. Furthermore, at relatively high concentrations, the very close packing of the nano-reinforcements limits the free space needed for them to rotate and align when subjected to the applied AC electric-field. The conductivity of the nanocomposites with aligned nano-reinforcements is significantly higher than that for the nanocomposites with randomly-oriented nano-reinforcements. However, the improvements in the conductivity of the CNF-epoxy nanocomposites are much more pronounced than for the GNP-epoxy nanocomposites. The conductivity of fully graphitized CNFs used in this study is reported to be about 2×10^6 S/cm [32], whereas the conductivity of the multi-layered GNPs is about 100 S/cm (perpendicular to surface) to 10^7 S/cm (parallel to surface) [33]. The anisotropic electrical conductivity of the GNPs would result in increased contact resistance between multi-layered GNP particles within a percolating network. This would lead to a lower conductivity improvement of the GNP-epoxy nanocomposites. Indeed, multi-layered graphite polymer composites have been reported to possess higher percolation thresholds with lower conductivity improvements [34] in comparison to their expanded graphite counterparts [35].

The influence of the type of nano-reinforcement, and its orientation in the epoxy, on the percolation threshold, V_{fc} , can be determined from the scaling-law equation [36] provided the nanofillers are well dispersed,

$$\sigma_{dc} = B(V_f - V_{fc})^n \quad (2)$$

where V_f is the volume fraction of the nano-reinforcement and B and n are material constants. **Table 1** lists the values of the percolation threshold and the associated material constants which are determined by curve fitting to Eq. 2 the experimentally measured DC conductivity data as a function of $(V_f - V_{fc})$ expressed as a weight fraction but otherwise according to the scaling-law equation. (It should be noted that the percolation threshold values and the corresponding constants are determined by searching for the highest R-value to establish the best curve fits.) The percolation thresholds for the nanocomposites with the randomly-oriented CNFs and GNPs are found to be 0.43 wt% and 0.95 wt%, respectively. The alignment of the CNFs and GNPs lowers the percolation thresholds to 0.25 wt% and 0.4 wt% respectively. Also, from **Fig 3**, the percolation thresholds can be confirmed by the appearance of the DC plateau at the nano-reinforcement content which represents the percolation threshold. Thus, these results clearly demonstrate that the epoxy nanocomposites with aligned nano-reinforcements require a significantly lower content of nano-reinforcement in order to achieve a conductive network, with the CNFs being more effective than the GNPs.

The percolation threshold and the corresponding material constants from **Table 1** can be used to design epoxy nanocomposite materials with the desired electrical properties using the scaling law equation and the frequency-dependent conductivity response of the epoxy with the following expression if $V_f \geq V_{fc}$

$$\sigma(\omega, V_f) = B(V_f - V_{fc})^n + A\epsilon_0\omega \quad (3)$$

where the dielectric response parameter (i.e. A) can be obtained by curve-fitting the conductivity results of the unmodified epoxy polymer. As can be seen from **Fig. 4b**, the model predictions are in good agreement with the experimental measurements.

Table 1: The value of the scaling law parameter determined by curve fitting the experimental conductivity results of the epoxy nanocomposites

Nano-reinforcement	V_{fc} (wt%)	n	B
CNF Aligned	0.25	2.65	6.6×10^{-3}
CNF Random	0.4	2.22	3.5×10^{-3}
GNP Aligned	0.43	1.10	6.0×10^{-6}
GNP Random	0.95	1.54	3.0×10^{-7}

Note: The value of parameter $A = 5.65$

3.3 Fracture energy studies

Fig. 5 shows typical applied load versus crack opening displacement curves for the epoxy nanocomposites measured from the DCB test specimen. The unmodified epoxy and all the CNF-epoxy nanocomposites (randomly-orientated or aligned) exhibited large and abrupt load drops with increasing displacement which is characteristic of unstable “stick-slip” type crack growth. The peak loads of the curves corresponded to the onset of crack growth, while the minimum loads corresponded to crack arrest. The GNP-epoxy nanocomposites with randomly-oriented or aligned GNPs at concentrations of 0.5 and 1.0 wt% also experienced unstable crack growth similar to that observed for the CNF-epoxy nanocomposites. However, at higher GNPs concentrations of 1.5 and 2.0 wt%, the fracture process was observed to transition to a more stable form of crack growth with smaller load drops. This suggests that different toughening mechanisms may operate in the CNF- or GNP-epoxy nanocomposites. The fracture energy values, G_{Ic} , for the onset of crack propagation were calculated using the maximum loads that were measured in accordance to ISO 25217 [28]. (The first peak of the load versus displacement curve was ignored to ensure that only subsequent values of the maximum loads, which were associated with crack initiation from relatively sharp (‘natural’) cracks were used to calculate G_{Ic} [28]). For all of the DCB tests bonded using the epoxy polymer nanocomposite and the unmodified epoxy, the locus of failure was along the centre of the polymer layer.

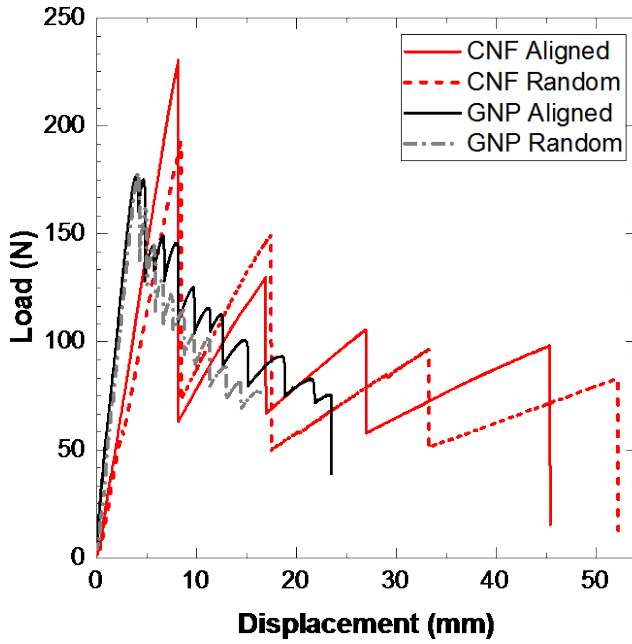


Fig 5. Typical load versus displacement curves for the epoxy nanocomposites containing 1.5 wt% of CNFs or GNPs (randomly-orientated and aligned).

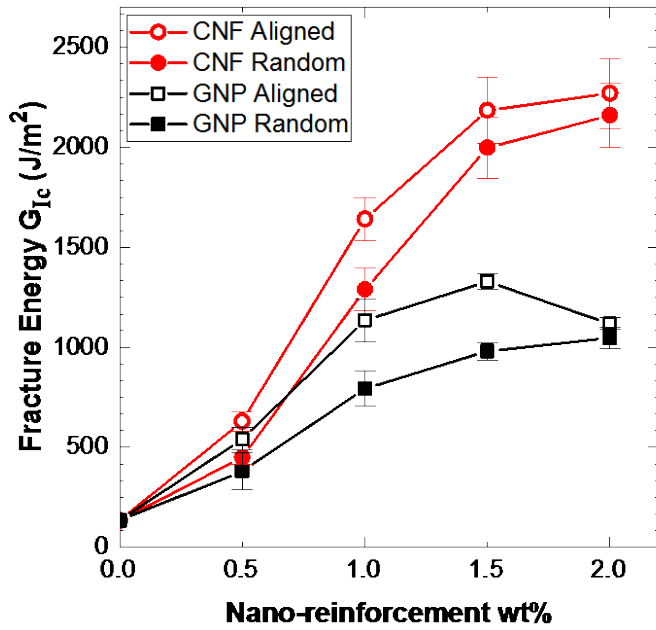


Fig 6. Effects of the nano-reinforcement concentration, shape and orientation on the fracture energy of the epoxy nanocomposites.

Fig 6. shows the effects of the weight fraction and orientation of the CNF and GNP nano-reinforcement on the fracture energy, G_{Ic} . The fracture energy increases almost linearly up to a nano-reinforcement concentration of 1.5 wt%, although no further improvements occurs at the highest concentration of 2.0 wt% due to agglomeration and restricted capacity to rotate the nano-reinforcement in the case of the aligned particles. Alignment of the CNFs and GNPs resulted in an additional toughening effect, with the fracture energies being respectively 25% and 40% higher for the nano-reinforcement

concentrations under 1.5 wt%. The toughening mechanisms responsible for the improvements in the measured toughness are discussed in the following section.

3.4 Toughening Mechanisms

Fractographic analyses of the DCB specimens provided a significant insight into the toughening mechanisms responsible for the improvements in the fracture energy of the epoxy nanocomposites. As shown in **Fig. 7a**, the unmodified epoxy exhibited a smooth and featureless crack surface indicative of brittle fracture. In comparison, the fracture surfaces of the DCB samples containing CNF-epoxy nanocomposites (at all concentrations) and GNP-epoxy nanocomposites (with contents of 0.5 and 1.0 wt%) exhibited a stick-slip crack propagation with distinct stress-whitening of the epoxy in the regions of crack initiation and arrest, as shown in a representative fracture surface in **Fig. 7b₁**. The stress-whitening arises from plastic deformation associated with the crack initiation process. The lengths of these stress-whitening bands increased with increasing concentration of the nano-reinforcements and hence correlate with the observed increases in the values of their fracture energy. For GNP-epoxy nanocomposites with a nano-reinforcement concentration of 1.5 and 2.0 wt%, the crack propagation mode was observed to transition from stick-slip to stable growth, with distinct stress-whitening extending along the entire fracture surface as shown in **Fig. 7b₂**. As shown in **Fig 7 c-f**, from SEM studies, patterns of tear marks were visible in the stress-whitened regions, which provide evidence of plastic deformation of the epoxy. These tear marks indicate that the crack propagation became more tortuous, with the severity of the tear marks increasing with increasing concentration of the nano-reinforcements.

The fracture energy of the epoxy nanocomposites is increased by both intrinsic toughening processes ahead of the crack tip together with extrinsic toughening behind the crack front. In **Fig. 8**, a significant number of relatively large voids are visible around both the CNF and GNP nano-reinforcements in the process zone immediately ahead of the crack. These voids are indicative of high-strain plastic flow of the epoxy in the process zone. The epoxy void growth mechanism occurs when the triaxial stress-field ahead of the crack tip is sufficiently high to cause debonding of the nano-reinforcements from the epoxy. A large amount of plastic strain energy is absorbed via debonding, initiation and growth of the voids, and this contributes to the increased fracture energy of the epoxy nanocomposites. The volume content of voids increased with the nano-reinforcement content, and this would account in part for the increased fracture energy of the nanocomposites with increasing CNF or GNP content. Indeed, for rubber- and nanosilica-toughened epoxies, this plastic void growth mechanism significantly increases the fracture toughness [37,38]. Void growth occurred in the nanocomposites with randomly-orientated or aligned nano-reinforcements. However, the voids around the CNFs were significantly larger than around the GNPs, and this would account for the higher fracture energy of the CNF-epoxy nanocomposites.

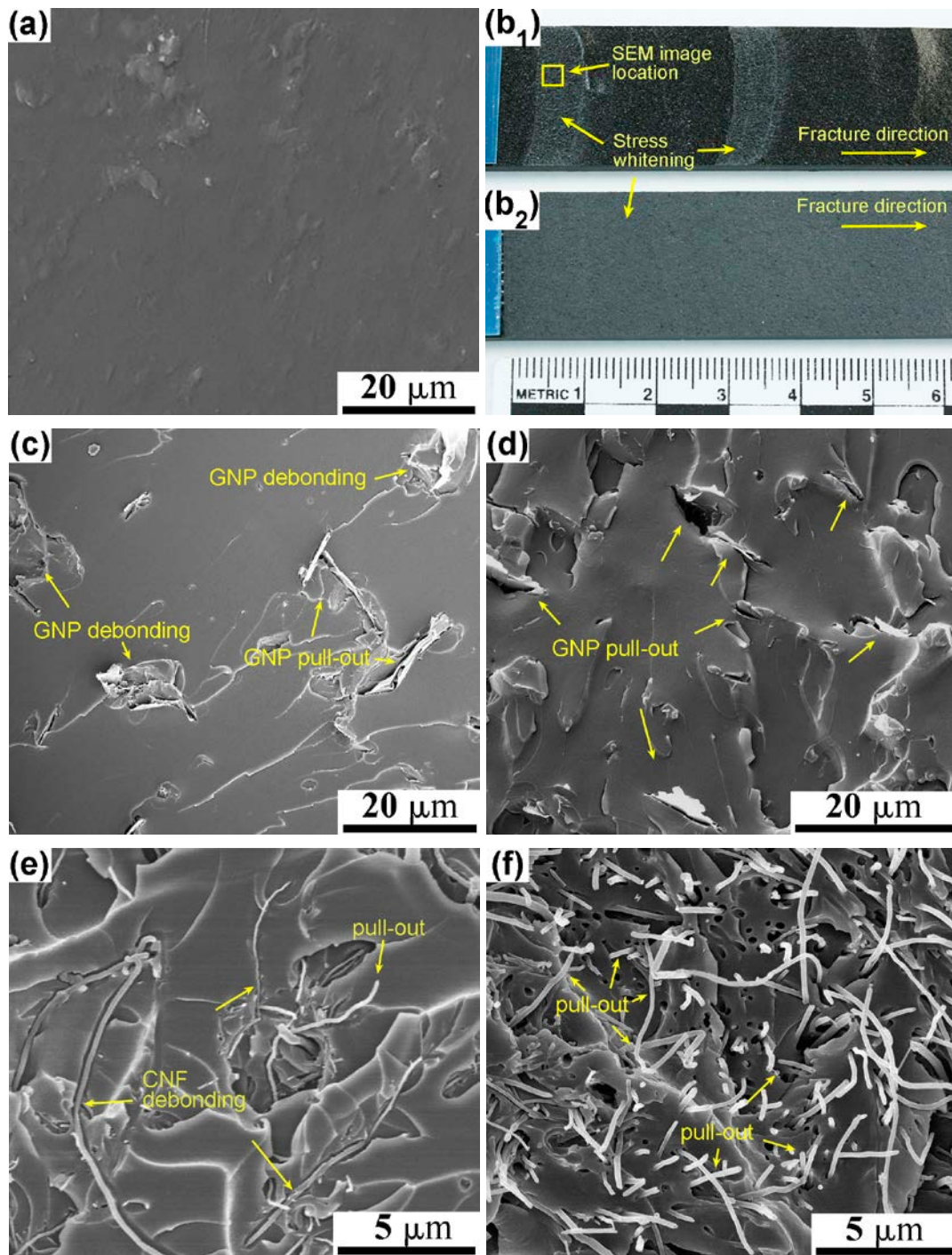


Fig 7. (a) SEM image of the fracture surface of unmodified epoxy polymer; photograph of the fracture surface of epoxy nanocomposites with (b₁) 1.5 wt % aligned CNFs and (b₂) 1.5 wt% aligned GNPs; SEM images of the fracture surface of epoxy nanocomposites containing (c) 1.5 wt% randomly-orientated GNPs; (d) 1.5 wt% aligned GNPs; (e) 1.5 wt% randomly-orientated CNFs; and (f) 1.5 wt% aligned CNFs.

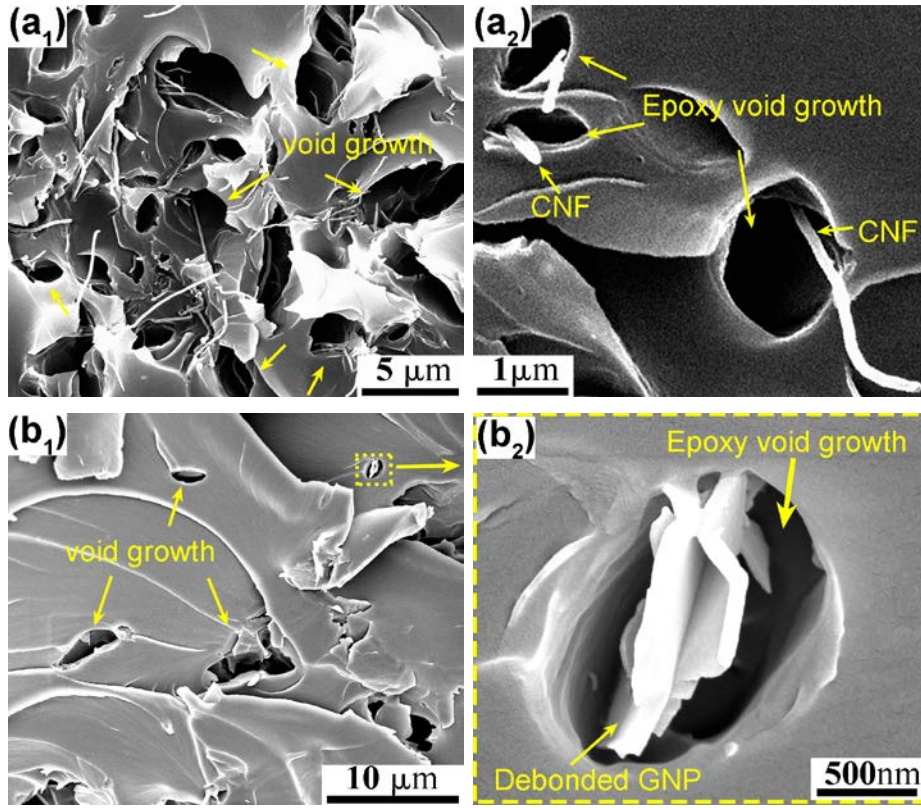


Fig 8. Representative SEM images of the fracture surfaces of the region immediately ahead of the crack front of the epoxy nanocomposites containing, (a₁) and (a₂) 1.5 wt% of CNFs which are randomly-oriented; (b₁) 1.5 wt% GNPs which are randomly-oriented and (b₂) is inset of b₁ at higher magnification.

The epoxy nanocomposites also exhibited extrinsic toughening processes in the forms of bridging and pull-out of the nano-reinforcements, as shown in **Fig. 9**. The formation of the crack bridging zone was observed to begin with the pull-out of the nano-reinforcements from the epoxy, as shown in **Fig. 9 a₁ and b₁**. As the crack front passes across the nano-reinforcements, they start to debond and pull-out from the side with the shorter embedded lengths on either side of the crack plane (see **Fig 9 a₂ and b₂**), and this toughening process shields the crack tip from the applied stress. The length of the nano-reinforcement bridging zone was longer for the GNP-epoxy nanocomposites compared to the CNF-epoxy nanocomposites due to the longer length of the GNPs, as shown in **Fig. 9 a₁ and b₁**. The frictional energy induced by the pull-out of nano-reinforcements from an epoxy is known to be a dominant toughening mechanism [39]. The relatively long nano-reinforcements rupture close to the crack plane since their embedded lengths is sufficiently long that they will break rather than pull-out (see **Fig 9 a₃ and b₃**). The absorbed strain energy associated with this tensile rupture of the nano-reinforcements contributes to the increases measured in the fracture energy.

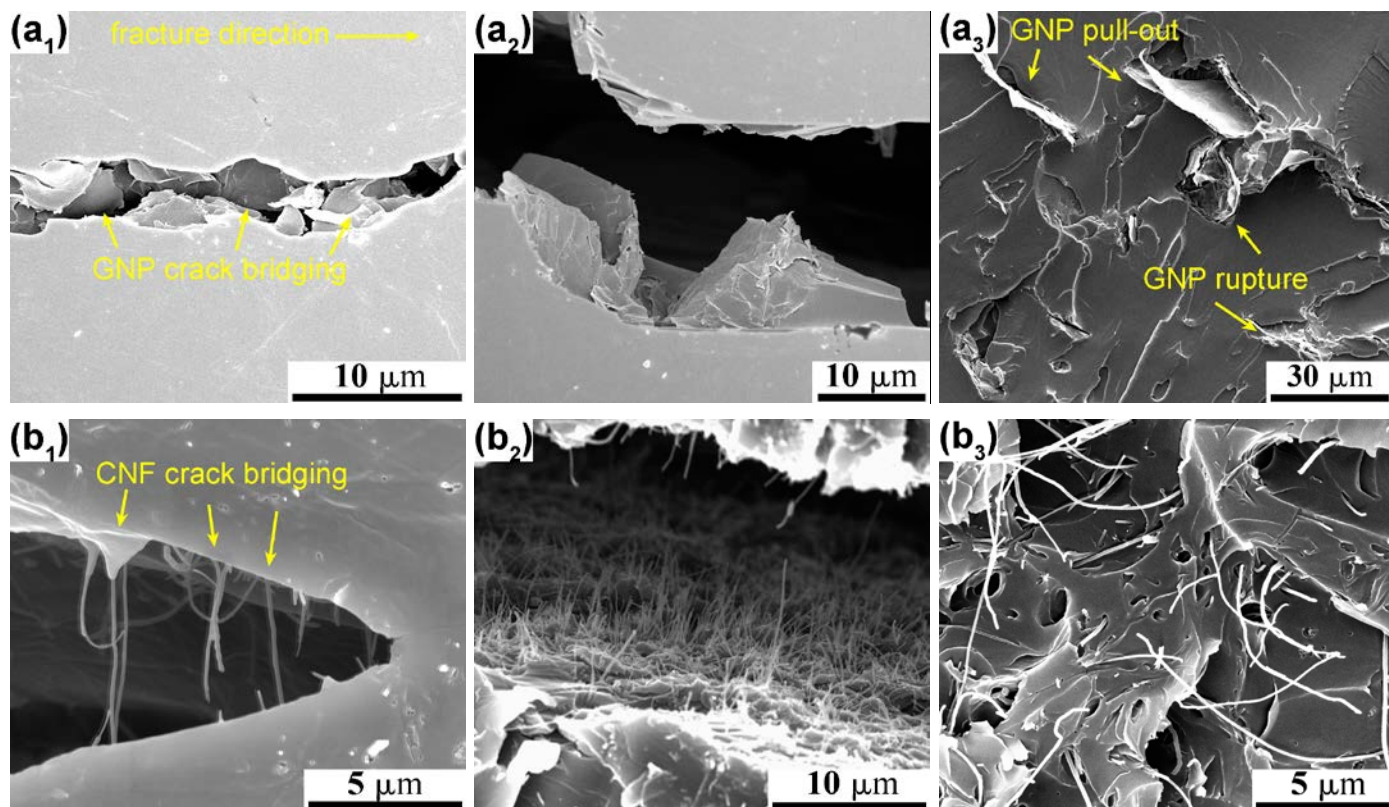


Fig 9. SEM images of the nano-reinforcement bridging the crack in epoxy nanocomposites containing; 1.0 wt% aligned GNPs (a₁) at the crack tip and (a₂) further down the crack wake; 1.0 wt% aligned CNFs (b₁) at the crack tip and (b₂) further down the crack wake. SEM image of the fracture surfaces of the 1.0 wt% of aligned nano-reinforcements in epoxy nanocomposite containing (a₃) GNPs and (b₃) CNFs nano-reinforcements.

The improvements to the fracture energy of the epoxy nanocomposites therefore result from the (a) frictional energy dissipated by pull-out of the nano-reinforcements, (b) rupture of the nano-reinforcements, (c) interfacial debonding of the nano-reinforcements, and (d) plastic void growth which initiates from the microvoids created by the debonded nano-reinforcements. While these toughening mechanisms were common to both the randomly-oriented and aligned nano-reinforcements, the contribution of each toughening mechanisms depends on the nano-reinforcement orientation. Alignment of the nano-reinforcements perpendicular to the crack path leads to a higher fraction of the nano-reinforcement participating in the toughening mechanisms. For randomly-oriented nano-reinforcements, the probability of the crack front encountering the nano-reinforcements depends on their orientation, and for an oblique angle above 60° to the crack plane this probability is less than 50% [15,40]. This would lead to fewer nano-reinforcements being pulled-out and contributing to the bridging and rupturing mechanisms. This is evident for the randomly-oriented nano-reinforcements shown in **Fig. 7c** and **e**, where a greater number of nano-reinforcements which were oriented parallel to the crack path have undergone debonding but without pulling-out. For the nanocomposites with aligned nano-reinforcements, as shown in **Fig 7d** and **f**, almost all the nano-reinforcements along the crack path have experienced debonding and pull-out. In addition, when

aligned normal to the direction of crack growth, the nano-reinforcements are more likely to bridge the crack faces and undergo tensile rupture, as may be seen in **Fig. 9**.

3.5 Fracture energy modelling

The primary toughening mechanisms operative in the nanocomposites were identified as (a) plastic void growth initiated by the debonded nano-reinforcements in the process zone ahead of the crack, (b) debonding and pull-out of the nano-reinforcements, and (c) bridging and rupture of the nano-reinforcements behind the crack tip. Assuming the application of continuum mechanics is valid at the nanoscale and the interfacial stress between the nano-reinforcement and epoxy is constant, then the energy dissipated by the pull-out of two-dimensional platelets such as GNPs can be calculated using the conventional expression for particle pull-out [41]:

$$\Delta G_{pull-out} = N 2(t + W) \tau_G l_{po}^2 \quad (4)$$

where t , W , l_{po} are the thickness, width and pull-out length of the GNPs respectively and τ_G is the interfacial shear strength. The parameter N is the total number of GNPs per unit area of crack surface, which is related to their volume fraction, V_f , via:

$$N = \frac{GNP \text{ volume}}{\text{volume per GNP}} = \frac{l V_f}{l A_{GNP}} = \frac{V_f}{A_{GNP}} = \frac{V_f}{t W} \quad (5)$$

where A_{GNP} and l are the cross-sectional area and the average length of the GNPs in the epoxy, respectively. Substituting Eq.(5) into Eq.(4) gives:

$$\Delta G_{pull-out} = \frac{2V_f (t+W) \tau_G l_{po}^2}{t W} \quad (6)$$

The GNP pull-out length l_{po} is difficult to determine with any high degree of accuracy from the SEM micrographs of the fracture surfaces. However, the pull-out length can be estimated in a similar way to the determination of the critical fibre length given by the classical Kelly-Tyson approach [42] where:

$$l_c = \frac{\sigma t W}{(t+W) \tau_G} \quad (7)$$

where σ is the tensile strength of the GNP. GNPs with lengths exceeding the critical length given by Eq.(7) are expected to fracture across the crack plane, since their embedded lengths on either side of the crack plane are sufficiently long for the stress in the GNP to build-up to cause their rupture. Therefore, the longest pull-out length without breaking is equal to half the critical length of the GNPs embedded in the epoxy:

$$l_{po} = \frac{t W \sigma}{2 (t+W) \tau_G} \quad (8)$$

Considering the GNP properties as supplied by the manufacturer and with the experimentally measured interface strength between GNP and the epoxy matrix being ~ 2.3 MPa [43], the GNP pull-out length is estimated to be about $8.7 \mu\text{m}$. This value is similar to the value determined from SEM observations of the

length of GNPs bridging the crack, as shown in **Fig. 9 a₁** and **a₂**. Substituting Eq.(8) into Eq.(6) gives the expression for the energy dissipated during pull-out of the GNPs:

$$\Delta G_{pull-out} = \frac{V_f t W \sigma^2}{2 (t+W) \tau_G} \quad (9)$$

The increase in fracture energy due to crack bridging by the GNPs is equal to the energy required to pull-out the bridging GNPs from the epoxy, and is therefore accounted for by $\Delta G_{pull-out}$ [44]. However, the energy associated with the elastic deformation of the GNPs up to their tensile failure stress is given by:

$$\Delta G_{rupture} = \frac{V_f l \sigma \varepsilon_{max}}{2} = \frac{V_f l \sigma^2}{2 E_G} \quad (10)$$

where E_G and ε_{max} are the Young's modulus and the tensile failure strain of the GNPs, respectively.

In addition, the GNPs debond from the epoxy prior to the pull-out process. The energy due to interfacial debonding can be derived using the same approach as that developed for debonding of fibres given by Hull [45]:

$$\Delta G_{db} = \frac{2V_f (t+W) l_{po} G_i}{t W} \quad (11)$$

where G_i is the interfacial fracture energy between the GNPs and epoxy.

Plastic void growth in the process zone ahead of the crack, which is initiated by debonding of the GNPs from the epoxy, increases the intrinsic toughness of the nanocomposites. The fracture energy contribution from the plastic void growth mechanism can be calculated by considering the model proposed by Huang and Kinloch [46]:

$$\Delta G_v = \left(1 + \frac{\mu_m}{\sqrt{3}}\right)^2 (V_{void} - V_f) \sigma_y r_{yu} K_{vm}^2 \quad (12)$$

where μ_m is a material constant allowing for the pressure dependency of the yield stress and K_{vm} is the maximum stress concentration for the von Mises stresses around a debonded GNP [22]. The parameters σ_y and r_{yu} are respectively the tensile yield stress and the plastic zone size at fracture of the unmodified epoxy. The plastic zone size is given by:

$$r_{yu} = \frac{1}{6\pi} \frac{E_m G_{cu}}{(1-\nu^2) \sigma_y^2} \quad (13)$$

where G_{cu} is the fracture energy, E_m is the tensile modulus and ν is the Poisson's ratio of the unmodified epoxy. From SEM fractographic observations, the volume fraction of voids, V_{void} , is estimated by assuming their shape to be an ellipsoid with their semi-major axis being equal to the average half width of the GNPs and their semi-minor axis being equal to four times the average GNP thickness as follows, noting $V_f = Nwt$

$$(V_{void} - V_f) = \left(N\pi(4t)\frac{w}{2} - Nwt\right) = V_f (2\pi - 1) \quad (14)$$

By combining the different energy terms given above, the fracture energy of the epoxy nanocomposites reinforced with 2-dimensional nano-reinforcements can be calculated from the following expression:

$$G_{Ic} = G_{CU} + \frac{V_f t W \sigma^2}{2(t+W) \tau_G} + \frac{V_f l \sigma^2}{2 E_G} + \frac{2V_f (t+W) l_{po} G_i}{t W} + \left(1 + \frac{\mu_m}{\sqrt{3}}\right)^2 [V_{void} - V_f] \sigma_y r_{yu} K_{vm}^2 \quad (15)$$

Similarly, the model for estimating the improvements in the fracture energy of the CNF epoxy nanocomposites was presented in our previous study by considering the conventional theories for fibre reinforcements [10]. For comparison with the two-dimensional GNPs given by Eq.(15), the model for the fracture energy, G_{Ic} , of one-dimensional CNF-epoxy nanocomposites is outlined below

$$G_{Ic} = G_{CU} + \Delta G_{pull-out} + \Delta G_{rupture} + \Delta G_{db} + \Delta G_v \quad (\text{for CNFs}) \quad (16)$$

$$G_{Ic} = G_{CU} + \frac{V_f \sigma_f^2 d_f}{8 \tau_f} + \frac{V_f \sigma_f^2 l_f}{2 E_f} + \frac{V_f l_{po} G_i}{d_f} + \left(1 + \frac{\mu_m}{\sqrt{3}}\right)^2 [V_f \left(\frac{d_v^2}{3 d_f^2} - 1\right)] \sigma_y r_{yu} K_{vm}^2 \quad (\text{for CNFs}) \quad (17)$$

where l_f and d_f are the length and diameter of the CNFs.

Table 2. List of values for the various parameters used in the analytical modelling studies.

Parameter	Symbol	Unit	Value	Source
CNF diameter	d_f	nm	70-200	[25]
GNP thickness	t	nm	1-20	[33]
GNP width	W	μm	25	[33]
CNF strength	σ_f	GPa	8.7	[25]
GNP strength	σ	GPa	5	[33]
Young's modulus of the CNF	E_f	GPa	320	[47]
Young's modulus of the GNP	E_G	GPa	1000	[47]
Density of the CNF	ρ_f	kg/m^3	1400	[25]
Density of the GNP	ρ	kg/m^3	2200	[33]
GNP/epoxy interface strength	τ_G	MPa	2.3	[43]
Density of unmodified epoxy	ρ_m	kg/m^3	1011	[24]
Tensile yield strength of unmodified epoxy	σ_y	MPa	50.5	[24]
Young's modulus of unmodified epoxy	E_m	GPa	3.17	[24]
Pressure dependent yield stress constant	μ_m	-	0.2	[46]
Maximum von Mises stress concentration	K_{vm}	-	2.11	[22]

Although the values for the interface strength τ_f between the CNF and epoxy are reported to be as high as 170 MPa [48], the value is in fact limited by the shear strength of the epoxy, which is approximately half that of the tensile yield stress using the Tresca yield criterion, giving a value of 25 MPa. The interfacial

fracture energy G_i associated with debonding of the CNFs from the epoxy has been measured to be 3.3 J/m^2 [49]. At present there are no reports on the interfacial fracture energy between GNPs and epoxy. Therefore, a similar value for the interfacial fracture energy between CNFs and epoxy was used to estimate the energy dissipated during debonding of GNPs. The volume of the voids around the CNFs is assumed to be a truncated cone with the inner diameter equal to the diameter of the CNFs and the larger void diameter, d_v , is determined from the SEM images to be approximately seven times. The values of all other input parameters used to calculate the fracture energy of the epoxy nanocomposites are given in **Tables 2**. The predictions from the model and a comparison with the experimental results are discussed in the following section.

3.6 Results of the fracture energy modelling

A comparison of the theoretical model predictions with the experimentally measured values of the fracture energies is shown in **Fig. 10**. Good agreement can be seen between the experimental results and the calculated fracture energies for the highest CNF diameter (200 nm) and GNP thickness (20 nm). The model is particularly sensitive to the diameter or thickness of the nano-reinforcements; larger dimensions enable longer pull-out lengths (see Eq. 7-9) leading to a greater increase in the degree of extrinsic toughening. The results shown in **Fig. 10** confirm the primary toughening mechanisms proposed for the epoxy nanocomposites modified using randomly-oriented or aligned nano-reinforcements. The calculated contributions to the improvement in the fracture energy from each of the toughening mechanisms are given in **Table 3**. Pull-out of the nano-reinforcements and void growth are the two most dominant toughening mechanisms, accounting for the majority of the fracture energy enhancement for all the epoxy nanocomposites. A notable difference between the modelling results for the CNF- and GNP-epoxy nanocomposites was that the intrinsic toughening due to void growth was more pronounced in the CNF-epoxy nanocomposites. In contrast, the extrinsic toughening due to GNP pull-out was significantly more dominant in the GNP-epoxy nanocomposites, accounting for almost four times the intrinsic energy dissipation via void growth in the epoxy around the GNPs. This explains the transition to more stable fracture behaviour that was measured by DCB testing for the 1.5 wt% and 2.0 wt% GNP-epoxy nanocomposites. In these nanocomposites, the more pronounced extrinsic toughening in the form of pull-out and crack bridging by the GNPs was more effective at retarding crack growth leading to a more stable fracture process. By contrast, the CNF-epoxy nanocomposites absorbed a higher amount of energy in the process zone ahead of the crack via void growth, leading to a greater improvement in its intrinsic toughness. This is an interesting finding, as it enables the selection of the appropriate type of nano-reinforcement for the materials design of nano-reinforced polymers in order to achieve the desired fracture properties. One-dimensional nano-reinforcements such as CNFs may be more beneficial in resisting the initiation of fracture in the event of impact damage, whereas two-dimensional nano-reinforcements such as GNPs may be more favourable for designing materials with a greater resistance to the unstable growth of cracks.

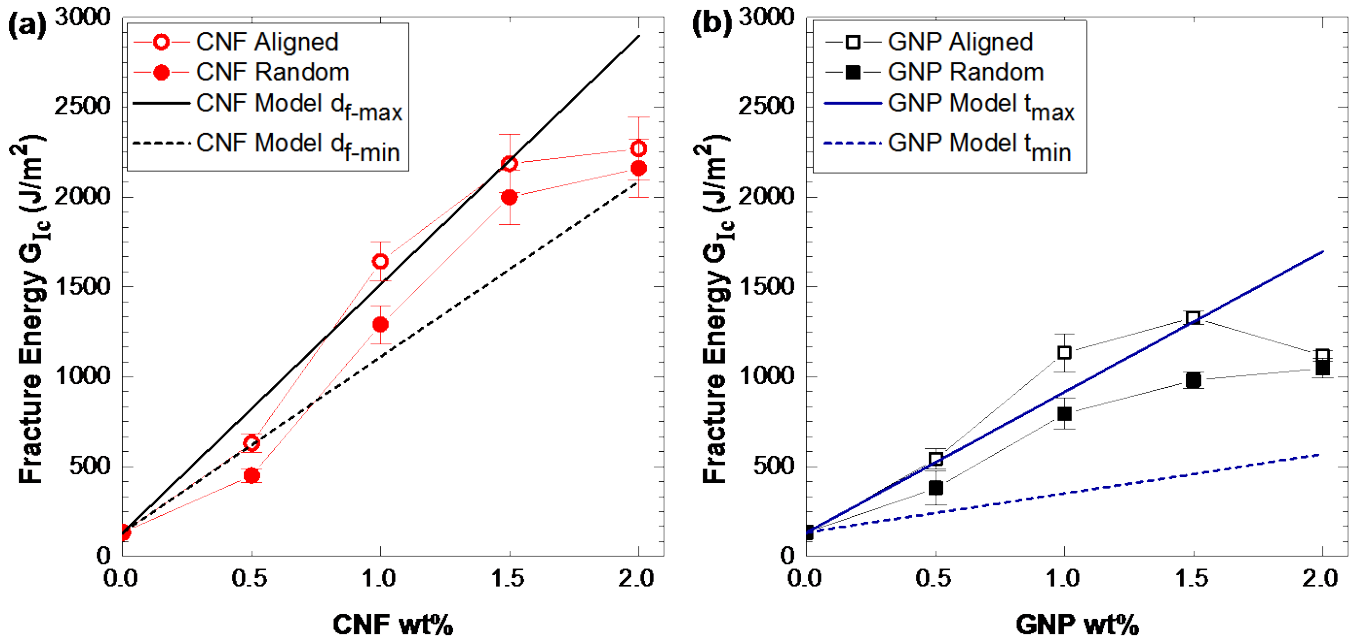


Fig 10. Comparison of the experimental fracture energies and theoretically calculated fracture energies (for the aligned nano-reinforcements) as a function of (a) CNF and (b) GNP weight content in the epoxy nanocomposites.

Table 3. Contributions to the fracture energy, G_{Ic} , of the epoxy nanocomposites for the various toughening mechanisms which were identified, as calculated from the analytical models for the highest values of the CNF diameter and GNP thickness.

Nano-reinforcement	Concentration (wt%)	$\Delta G_{pull-out}$ (J/m ²)	$\Delta G_{rupture}$ (J/m ²)	ΔG_{db} (J/m ²)	ΔG_v (J/m ²)
CNFs	0.5	311	10	1.2	369
	1.0	622	19	2.4	737
	1.5	933	29	3.5	1106
	2.0	1243	39	4.7	1474
GNPs	0.5	297	0.9	20	73
	1.0	595	1.7	39	146
	1.5	892	2.6	59	219
	2.0	1190	3.4	79	292

4. Conclusions

The effect of the carbon nano-reinforcement shape, orientation and concentration on the improvements observed in the electrical conductivity and fracture toughness of epoxy nanocomposite materials have been investigated. The application of an AC electric-field before the cure process of the resin can align CNFs or GNPs in the direction parallel to the external field. Compared to the unmodified epoxy, the improvements in electrical conductivity of the nanocomposites with aligned CNFs and GNPs were increased by about ten and seven orders of magnitude, respectively. Also, the percolation threshold of the nanocomposites containing aligned nano-reinforcements was about 50% lower than that of their randomly-orientated counterparts. The values of the fracture energy, G_{Ic} , of the nanocomposites containing 0.5 wt% of randomly-oriented one-dimensional CNFs or two-dimensional GNPs was improved by up to about 200%, compared to the unmodified epoxy. An additional improvement in fracture energy of up to about 40% was achieved by aligning the nano-reinforcement transverse to the crack growth direction. The efficacy of the alignment of the nano-reinforcement on the improvement in the electrical conductivity and the fracture energies of the nanocomposites was found to diminish at higher concentrations of the nano-reinforcement.

The large improvements in the fracture energy of the epoxy nanocomposites were due to toughening mechanisms involving (a) debonding of the nano-reinforcements, (b) the energy associated with the frictional pull-out of the nano-reinforcements from the epoxy, (c) crack bridging and rupturing of the nano-reinforcements, and (d) void growth around the debonded nano-reinforcements in the process zone. Fracture energy modelling revealed that the one-dimensional CNFs are more effective at increasing the intrinsic toughness in the form of epoxy void growth, whereas the two-dimensional GNPs are efficient at extrinsic toughening through pull-out and crack bridging of the GNPs.

The results from the present modelling studies were in good agreement with the experimental results and will enable the materials design of polymer nanocomposites, thereby resulting in the more rapid and cost-effective development of such novel materials.

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