Increasing the Fatigue Resistance of Epoxy Nanocomposites by Aligning Graphene Nanoplatelets

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ABSTRACT

Graphene nanoplatelets (GNPs) offer great potential for enhancing the multifunctional properties of epoxy polymers, including the cyclic-fatigue crack growth resistance. In the present work we investigate the effectiveness of electric-field alignment of GNPs in increasing the fatigue resistance of such epoxy nanocomposites. The GNPs were aligned in an uncured (liquid) epoxy resin by applying an alternating-current electric field during the curing process, before gelation of the epoxy. The fatigue properties of the cured epoxy containing both random and aligned GNPs were measured using double cantilever beam (DCB) specimens tested in displacement control over a range of cyclic energy release rates from the threshold condition (i.e. below which no fatigue crack growth was observed) to fast fracture. The results show that aligning the GNPs using an electric field yields a greater improvement in the fatigue crack growth resistance than obtained using randomly-orientated GNPs, particularly in the near threshold region. The resistance of the epoxy nanocomposites to fatigue crack growth was increased as the weight fraction of the GNPs was increased up to a certain level, beyond which there was no further improvement in the fatigue resistance. These improvements have been attributed to several toughening mechanisms which retard the fatigue crack growth in the epoxy nanocomposites, including debonding of the GNPs, epoxy void growth, crack deflection and branching of the main fatigue crack caused by microcracking induced by the presence of the GNPs, pull-out and crack bridging by the GNPs, and crack shielding by GNP debris particles behind the advancing fatigue crack tip. These toughening mechanisms become more active when the GNPs are aligned normal to the
direction of fatigue crack growth, which results in a higher fatigue resistance for the epoxy nanocomposites containing aligned GNPs than for those containing randomly-orientated GNPs.

**Keywords:** A. Nanocomposites; B. Fatigue; C. Graphene; D. Fractography

1 INTRODUCTION

Fibre reinforced composites, particularly those based on thermosetting polymer matrices, are known to suffer from a relatively low matrix-dominated fatigue resistance. Hence, fatigue-induced delamination under cyclic loads is a major design concern for such fibre composites, especially when existing airworthiness regulations [1] prescribe that aircraft composite structures must be designed for no growth, or slow and stable growth, under cyclic fatigue loadings so as to avoid fast fracture and potentially catastrophic failure [2–4]. To overcome such concerns, and therefore increase the use of fibre composites in safety-critical applications, significant efforts have focused on increasing the fatigue resistant properties of composite materials through the use of thermoplastic interleaves [5–7] and through-thickness reinforcement (e.g. using woven yarns and z-pins) [8–11]. A promising alternative technique to improve the interlaminar properties of composites is the addition of nanosized fillers to the polymer matrix, such as nanosilica particles [12,13], zinc oxide nanorods [14], nanosilica- and rubber-particle hybrids [15], carbon nanofibers [16–19] and carbon nanotubes (CNTs) [20–25]. For example, Blackman et al. [13] found that the fatigue resistance of an epoxy was increased by the addition of nanosilica particles, with the largest improvements occurring near the threshold stress intensity factor ($\Delta K_{th}$), below which no fatigue crack growth occurs. Hsieh et al. [23] reported that the threshold energy release rate ($G_{th}$) in an epoxy was approximately doubled with the addition of a small concentration (i.e. 0.5 wt%) of CNTs. Hsieh and colleagues attributed this improvement to the toughening mechanisms of debonding and pull-out of the CNTs, as well as localised plastic yielding and void growth in the polymer matrix.

Graphene nanoplatelets (GNPs) have recently attracted considerable interest as a highly effective filler to improve the multifunctional properties of epoxy polymers and fibre composites, including
mechanical, electrical and thermal properties [26–34]. A low concentration of GNPs, typically under 1-2 wt%, has been found to be effective in substantially increasing the fatigue performance [35–38]. For example, Rafiee et al. [35] found that GNPs extended the fatigue life of polymers by retarding the crack growth rate. They measured up to a 40-fold reduction of the fatigue crack growth rate due to the nanoparticles. Yavari et al. [36] reported a 1200-fold increase of the flexural fatigue life and a 3- to 5-fold increase of the uniaxial tensile fatigue life of epoxies containing a hybrid combination of GNPs and carbon nanofibres. One common feature to all these studies is that the GNPs were randomly oriented. However, research into other types of nanocomposites have demonstrated that aligning the nanoparticles normal to the crack growth direction can further enhance the toughness and fatigue resistance [16,17,39–41]. For example, carbon-based nanoparticles can be readily aligned in a preferred orientation by applying an external electric field [16,17,39] or magnetic [40,41] field to the nanocomposite before the thermosetting polymer has gelled.

The present paper therefore describes an investigation into whether the electric field alignment of GNPs improves the fatigue crack growth properties of epoxy nanocomposites compared to randomly-orientated GNPs. An unmodified epoxy (i.e. without GNPs) and epoxy-based nanocomposites containing different concentrations of GNPs (i.e. 0.5, 1.0, 1.5, 2.0 wt%), which were randomly-orientated or aligned using an electric field, were fatigue tested under mode I cyclic loading, using displacement control conditions, over a range of cyclic energy release rates. The toughening mechanisms under fatigue loading of the epoxy nanocomposites containing the GNPs in the random and aligned conditions were also identified. Using these approaches, the optimum alignment and concentration of GNPs have been identified to provide improved fatigue-resistant epoxies that could be used as the matrix phase of fibre reinforced polymer composites.

2 MATERIALS, ELECTRIC ALIGNMENT AND FATIGUE TESTING

2.1 Fabrication of Nanocomposites

The process used to manufacture the epoxy nanocomposite specimens containing GNPs for mode I fatigue testing is shown in Figure 1. Multi-layer GNPs (Type M-25 supplied by XG Sciences) with an
average thickness of 6-8 nm (ca. ~18 layers), an average diameter of 25 µm, and a surface area of 120-150 m²/g were used. The GNPs were mixed into a liquid epoxy resin consisting of a blend of Bisphenol A and Bisphenol F (‘105’ from West System, Australia). At this stage of the process the liquid hardener was not added to the epoxy. Different weight fractions of GNPs were manually mixed in the resin for five minutes, and then passed through a three-roll mill (Dermamil 100) to obtain a good dispersion (Figure 1a). The liquid epoxy-GNP mixtures were passed six times through the mill, with the roll speed incrementally increasing and the roller gap decreasing with each pass, with the final pass performed at a speed of 150 rpm using a roller gap distance of 20 µm. Following this, the hardener, consisting of a modified aliphatic polyamine (‘206’ from West System, Australia), was mixed with the epoxy resin at a weight ratio of 1:5.36. Epoxy-based nanocomposites were produced with 0.5, 1.0, 1.5 and 2.0 wt.% GNPs. It was observed that the dispersion of GNPs became more difficult at the highest content (i.e. 2.0 wt%) when they started to agglomerate.

The liquid epoxy nanocomposites were used to form a relatively thick adhesive layer (i.e. 3 mm) between two carbon fibre-epoxy (CFRP) composite laminates to create double cantilever beam (DCB) test specimens for fatigue testing (see Figure 1). The laminates were fabricated using 12 plies of unidirectional T700 (24K) carbon-epoxy prepreg (VTM264 supplied by Cytec Industrial Materials). The composite was cured and consolidated in an autoclave at 120°C and 620 kPa (90 psi) for one hour according to the manufacturer’s recommendation. The cured laminates were 0.5 mm thick with a carbon fibre content of about 58 vol%. To aid subsequent adhesive bonding with the epoxy nanocomposites, the surfaces of the laminates were lightly grit-blasted using glass beads, polished with sand-paper, and then cleaned with isopropyl alcohol.

2.2 Electric Field Alignment of the Graphene Nanoplatelets

The CFRP composite laminates act both as substrates to form the adhesively-bonded joint and as electrodes to align the GNPs in the through-thickness direction of the liquid nanocomposite layer (Figure 1c). A sinusoidal alternating current (AC) electric field with a strength of 25 V/mm and a frequency of 10 kHz was applied between the two composite substrates using a Tektronix CFG250
generator and a Krohnite 7602M amplifier. (These conditions were selected based upon previous work [16] using carbon nanofibres). The electrical field was applied continuously to the epoxy nanocomposite layer for two hours, during which period it transformed from a liquid via polymerisation and cross-linking to a gel and then a solid. (The total curing time was for 48 hours at room temperature (i.e. 25 °C), in accordance with the resin supplier’s recommendations.) The GNPs were initially randomly oriented, but the nanoplatelets rotated and aligned in the direction of the electric field while suspended in the liquid epoxy before gelation and solidification. This is shown by optical micrographs presented in Figure 2 of a liquid epoxy nanocomposite shortly after (1 minute) and after an extended period (20 minutes) of exposure to the electric field. The initially randomly oriented and evenly dispersed GNPs aligned into a highly-ordered network in the direction of the electric field. The GNPs joined together end-to-end to form a fine chain-like network which extended between the two electrodes. This state was retained as the epoxy underwent gelation and cure, thereby locking-in the aligned structure of the GNPs (Figure 2b). Similar chain-like networks have been observed with carbon nanofibres in a liquid epoxy following exposure to an electric field [16].

Histograms shown in Figure 2d compare the orientations of the GNPs in the random and aligned conditions. The orientation of the GNPs was measured from optical microscopy images of the nanocomposites. A grey-level thresh-holding technique (shown by the inset images in Figures 2a-2c) was performed to distinguish the GNPs from the epoxy matrix in accord with the instructions given in [42,43]. A directionality algorithm, using a 2D fast Fourier transform in ImageJ software, was then used to determine the orientation of the GNPs [43,44]. The so-called randomly-orientated GNPs actually do show some preferred aligned, and this is the result of the three-roll milling process rotating and aligning some of the nanoplatelets in the rolling direction. However, the GNPs exposed to the electric field show a much higher degree of alignment, but not all the nanoplatelets were fully aligned in the field direction.
2.3 Fracture Toughness Testing

The mode I fracture toughness of the unmodified epoxy and epoxy nanocomposites were determined using the DCB test in accordance with ISO 25217:2009 [45]. The DCB specimens consisted of a 3 mm thick epoxy layer (with or without GNPs) sandwiched between the two 0.5 mm thick CFRP composite substrates. The DCB test specimens were 230 mm long × 20 mm wide × 4 mm thick (Figure 1d). At least five replicate DCB tests were performed for the unmodified epoxy and the epoxy nanocomposites with different GNP concentrations, which were randomly-orientated or aligned (Figure 1e). A Teflon film (50 mm long × 50 µm thick) was placed at the mid-thickness of the epoxy-based layer before curing to act as the starter crack. The pre-cracked end of the DCB specimens were subjected to a monotonically increasing opening displacement which was applied at rate of 1 mm/min using a 10 kN loading machine (Instron 4466). The crack was forced to grow incrementally along the polymer layer in the DCB specimens by monotonically increasing the opening displacement, and then unloading to stop crack growth. At each increment the applied force \(P_c\), crack opening displacement \(\delta_c\) and crack length \(a\) values were measured. The crack length was measured using a travelling optical microscope located along one side of the DCB specimen. Using these data, the mode I strain energy release rate \(G_{IC}\) was calculated using the ‘corrected beam theory’ [45]:

\[
G_{IC} = \frac{3P_c\delta_c}{2b(a + |\Delta l|)}
\]

where \(b\) is the width of the DCB specimen and \(|\Delta l|\) is a compliance factor that corrects for vertical displacement and bending at the crack tip.

2.4 Fatigue Testing

Mode I interlaminar fatigue testing of the DCB specimens was performed according to the test methods described in ASTM E-647 [46]. The DCB specimens were tested under cyclic displacement control using a 3 kN fatigue testing machine (Instron E-3000). The cyclic crack opening displacement was applied using a sinusoidal waveform at a frequency of 5 Hz. The R-ratio, defined as the ratio between the minimum and the maximum crack opening displacements, was 0.5. The fatigue crack was
allowed to grow a short length (typically 0.9 mm-1.2 mm) under a constant amplitude fatigue load condition. At each increment of crack extension, the maximum applied force \((P_{\text{max}})\), the minimum applied force \((P_{\text{min}})\), the maximum crack opening displacement \((\delta_{\text{max}})\), the minimum crack opening displacement \((\delta_{\text{min}})\), and crack length \((a)\) values were recorded. Using these data, first, the maximum energy release rate \((G_{I\text{max}})\) and minimum energy release rate \((G_{I\text{min}})\) were calculated using the ‘corrected beam method’:

\[
G_{I\text{max}} = \frac{3P_{\text{max}}\delta_{\text{max}}}{2b(a + |\Delta l|)}
\]  
(2)

\[
G_{I\text{min}} = \frac{3P_{\text{min}}\delta_{\text{min}}}{2b(a + |\Delta l|)}
\]  
(3)

Using these data, the equivalent energy release rate \((\Delta G_{I\text{eq}})\) was calculated using [46,47]:

\[
\Delta G_{I\text{eq}} = \left(\sqrt{G_{I\text{max}}} - \sqrt{G_{I\text{min}}}\right)^2 = G_{I\text{max}}(1 - R)^2
\]  
(4)

where \(R = P_{\text{min}}/P_{\text{max}}\). The magnitude of \(\Delta G_{I\text{eq}}\) decreases with crack length under displacement control, which makes it relatively easy to measure the fatigue crack growth rate per cycle \((da/dN)\). The DCB joints always failed by cohesive crack growth in the unmodified epoxy or the epoxy nanocomposite adhesive layer.

2.5 Optical and Fractographic Studies

Preliminary validation of any alignment and chaining of the GNPs due to application of the electric field was performed using a LEICA DC300 optical microscope. The fracture surfaces and the sides of the specimens in the region of the crack tip, from the DCB tests were characterised using a scanning electron microscope (SEM). Either a FEI Verios 460L SEM or a Philips XL30 SEM was employed. The operating voltage and working distance were optimized to obtain clear images. All the specimens were cleaned using an ultrasonic bath for 1 minute in acetone and subsequently in ethanol. Specimens were then exposed for 2 minutes in a GATAN Solarus 950 H\textsubscript{2}O\textsubscript{2}-enabled plasma to gently remove any surface contamination. Finally, the specimens were gold coated before fractographic analysis to prevent the specimens charging under the electron beam.
3 RESULTS AND DISCUSSION

3.1 Quasi-static Studies

The values of $G_{IC}$ obtained are listed in Table 1. The results reveal that electric field-induced aligning of the GNPs increases the fracture toughness irrespective of the concentration of the GNPs present. This increase is greater than the increase achieved by the addition of randomly-oriented GNPs. For example, for the randomly-oriented GNPs nanocomposites, when compared to the unmodified epoxy, the average value of $G_{IC}$ increases from 0.165 kJ/m$^2$ to 0.336 kJ/m$^2$ for a concentration of 0.5 wt.% of GNPs, which represents an increase by a factor of approximately two. In comparison, alignment of the GNPs, for the same concentration, produces an increase of about three times (i.e. gives a $G_{IC}$ value of 0.451 kJ/m$^2$) compared to the unmodified epoxy. This trend of increasing $G_{IC}$ upon the addition of GNPs, and their alignment, continues until a concentration of 1.5 wt.% is reached. At this concentration, the maximum toughness ($G_{IC}$) improvement is observed, which is an increase of about nine times for an epoxy nanocomposite containing 1.5 wt.% of aligned GNPs, whilst a times eight increase is observed for the randomly-oriented GNPs at this concentration. The reason for no further increases in the values of $G_{IC}$ at the highest concentration of GNPs (i.e. 2.0 wt%) that was employed is suggested to be due to the significant agglomeration of the GNPs in the epoxy which was observed at this relatively high concentration.

3.2 Fatigue Studies

The fatigue crack growth rate curves are presented in Figure 3 for the unmodified epoxy and the epoxy nanocomposites containing different weight fractions of randomly-orientated or aligned GNPs. The curves show plots of the fatigue crack growth rate per cycle ($da/dN$) versus the equivalent cyclic strain energy release rate ($\Delta G_{Ieq}$) as defined by equation (4). The fatigue curves can be divided into three regions:

- Region A is the threshold region where the crack growth rates are very slow (typically below $\sim 10^{-5}$ mm/cycle);
• Region B is characterised by an approximately linear (i.e. Paris) relationship between \( \frac{da}{dN} \) and \( \Delta G_{eq} \) when both of these terms are plotted using logarithmic axes (typically between \(~10^{-5}\) and \(~10^{-2}\) mm/cycle);

• Region C refers to a fast fracture process where the crack growth rates accelerate rapidly with as the \( \Delta G_{eq} \) is increased further (i.e. \( \frac{da}{dN} \) values typically being above \(~10^{-2}\) mm/cycle).

The curves in Figure 3 were calculated using the Forman equation [48] to account for the effects of the threshold on the crack growth rate, as given by the following relationship [49]:

\[
\frac{da}{dN} = \frac{C[\Delta G_{leq} - \Delta G_{leq,th}]^m}{(1 - R)(\sqrt{G_{lc}} - \sqrt{\Delta G_{leq}})}
\]

(5)

where \( \Delta G_{leq,th} \) denotes the value of the threshold energy release rate below which no fatigue crack growth occurs, \( G_{lc} \) the adhesive fracture energy for fast fracture, and \( R \) is the R-ratio. The parameters \( C \) and \( m \) are the slope and exponent of the linear curve in the Paris region, respectively. The values of the quasi-static fracture toughness, \( G_{lc} \), and the fatigue parameters for the unmodified epoxy and the epoxy GNP nanocomposites are given in Table 1.

The results shown in Table 1 and Figure 3 reveal several interesting features. Firstly, that the addition of randomly-orientated GNPs to the epoxy improves the quasi-static fracture energy and the cyclic fatigue resistance. Indeed, up to a concentration of 1.5 wt%, the addition of randomly-orientated GNPs to the epoxy steadily increased the values of \( G_{lc} \) and \( \Delta G_{leq,th} \) and also retarded the crack growth rate at a given value of \( \Delta G_{leq} \) as the concentration of GNPs was increased.

Secondly, the addition of the randomly-orientated GNPs to the epoxy were very effective at retarding the rate of fatigue crack growth in the near threshold region, as evidenced by the rapid increase in the value of \( \Delta G_{leq,th} \) with increasing concentration of randomly-orientated GNPs, as shown in Table 1. In particular, the addition of 1.5 wt% of randomly-orientated GNPs increased the value of \( \Delta G_{leq,th} \) for the epoxy by \(~12\) times, compared to the unmodified epoxy.
Thirdly, as commented above, no further major increases in the values of $G_{lc}$ and $\Delta G_{eq.th}$, and the overall fatigue resistance, were observed upon the addition of randomly-orientated GNPs at a concentration of 2.0 wt% compared to 1.5 wt%. Indeed, the value of $G_{lc}$ significantly decreased when using a concentration of 2.0 wt% of GNPs. These observations were due to the significant agglomeration of the GNPs that was observed when added at the higher concentration of 2.0 wt%. It is known that poor dispersion due to agglomeration is a common problem when nanoparticles are used at relatively high concentrations in polymers [12, 28, 39,50] and this often adversely affects their ability to improve the properties of polymers [17, 30, 35,39].

Fourthly, electric-field alignment of the GNPs normal to the crack growth direction further improved the fatigue resistance of the epoxy nanocomposites, as shown in Figure 3 and Table 1. Compared to the epoxy nanocomposite containing randomly-orientated GNPs, aligning the GNPs provided the greatest improvements in the fatigue resistance at relatively slow crack growth rates in the near-threshold region (i.e. Region A). Table 1 shows that the values of $\Delta G_{eq.th}$ were significantly higher when the GNPs were aligned to be normal of the fatigue crack growth direction, compared to the randomly-orientated GNPs. However, as for the randomly-orientated GNPs, no significant increases in the values of $G_{lc}$ and $\Delta G_{eq.th}$, and the overall fatigue resistance, were measured for the 2.0 wt% aligned GNPs. Again, this was due to the agglomeration of the GNPs, which also greatly hinders the subsequent alignment of the GNPs, when the GNPs were added at this highest concentration of 2.0 wt%.

3.2 Fractographic Studies and Toughening Mechanisms

Fractographic examination of the nanocomposites during and following cyclic DCB testing revealed that the GNPs induced multiple toughening mechanisms in the epoxy nanocomposites which increase the fracture energy and the fatigue resistance of the epoxy. These increases stem from an increase in
the type and extent of the toughening mechanisms that are induced by the GNPs, and these are discussed in detail below.

Considering the intrinsic toughening mechanisms, cross-sectional images, taken using the scanning electron microscope, of the region surrounding the fatigue crack tip in the unmodified epoxy and nanocomposites containing randomly-orientated or aligned GNPs are presented in Figures 4 and 5. The unmodified epoxy has a well-defined fatigue crack with no observable damage ahead of the crack tip. While a small plastic zone exists at the crack tip, no physical damage (e.g. micro-cracks) can be observed within this zone. In contrast, a process zone ahead of the main fatigue crack in the epoxy nanocomposites containing randomly-orientated or aligned GNPs contains clearly visible micro-cracking (see Figures 4b & c and 5a). The extent of micro-cracking within this zone increased with the concentration of GNPs, and such micro-cracks developed at many of the GNPs present in the process zone. These micro-cracks form due to the presence of the relatively high triaxial (hydrostatic) stress state that exists within the process zone. Such a stress state induces (a) separation of the individual graphene layers in the GNPs and/or (b) debonding of GNPs from the epoxy matrix (see Figures 5b & c and 6). These two options for the creation of the microcracks arise since, firstly, the graphene sheets within a GNP are weakly bonded to each other, and therefore readily separate under the triaxial stresses which exist within the process zone. Secondly, the elastic modulus of the GNPs is much higher than the epoxy matrix, and consequently localised stress concentrations may be generated at the GNP-epoxy interface that can lead to debonding. The discrete micro-cracks that are formed within the process zone coalesce close to the main fatigue crack front and lead to deflection and branching of the crack tip (see Figures 4b & 4c and Figure 5a). Further, this crack deflection and branching caused the main fatigue crack in the nanocomposites to follow a more tortuous crack path than the unmodified epoxy. This is evident from the increased roughness of the fracture surfaces of the epoxy nanocomposite, which increases with an increase in the concentration of GNPs, as shown in Figure 7. Such deflection and branching of the crack tip are indeed known [39] to act as toughening mechanisms.
Improvements in the fatigue resistance of the epoxy nanocomposites also resulted from new extrinsic mechanisms operating behind the main crack front, that can only arise in the presence of the GNP s. The GNPs were observed to pull-out and bridge the fatigue crack when aligned normal to the crack growth direction, as shown in Figure 8. Due to their high stiffness and strength, the bridging GNPs generated traction loads which contribute to an improvement to the fatigue resistance of the nanocomposites. Crack bridging occurred more frequently when the GNPs were aligned normal to the direction of fatigue crack growth, and this, in part, accounts for the higher fatigue resistance of the aligned GNP nanocomposites. The bridging GNPs are eventually ruptured, or completely pulled-out, of the epoxy matrix under the cyclic loads, as shown in Figure 9, and this pull-out process generates a frictional traction load which will further enhance the fatigue resistance. The pull-out traction loads will be greater when the GNPs are aligned normal to the crack growth direction. This will result in a higher fatigue resistance for the aligned GNP nanocomposites compared to the randomly-orientated GNP nanocomposites. However, due to the relatively short length of the GNPs (i.e. average size ~ 25 µm) they were only capable of bridging the fatigue cracks for a short distance behind the main front before being pulled-out under the applied cyclic loads.

Finally, the fractographic studies revealed the presence of debris particles inside the fatigue crack, and behind the advancing crack tip, in the nanocomposites, as shown for example in Figure 10. Such debris particles were not observed in the unmodified epoxy. It appears that due to the extensive amount of crack-tip branching that occurred in the epoxy nanocomposites, which arose from the microcracking within the process zone caused by presence of the GNPs, some fragments of the material broke away and became wedged between the surfaces of the advancing fatigue crack. The amount of such debris inside the fatigue crack increased with the concentration of GNPs, due to the increased amount of crack tip branching that occurred as the concentration of GNPs was increased. Debris particles are known [51–53] to induce extrinsic toughening by shielding the crack tip, particularly when the crack opening is small, i.e. less than the particle size. This shielding effect essentially arises because the debris particles induce physical contact between the mating crack surfaces during crack closure within a single fatigue load cycle (i.e. as the value of $G_{\text{Imin}}$ is
approached). This effectively reduces the stress concentration acting at the crack tip and therefore retards the rate of fatigue crack growth. This toughening mechanism is clearly most effective in Region A when the crack opening displacements are relatively small and so crack closure is readily prevented from occurring by the presence of the debris particles. This toughening mechanism therefore retards the fatigue crack growth rate in the GNP nanocomposites (for both randomly-orientated and aligned GNPs) compared to the unmodified epoxy polymer in Region A. However, as the value of $\Delta G_{eq}$ is increased further, the minimum crack opening displacement exceeds the size of the debris particles and thus there is a diminished, and eventual absence of, any crack shielding effect for the GNP epoxy nanocomposites.

In summary, the presence GNPs in the epoxy promote an enhancement of the fatigue resistance in the epoxy nanocomposites via inducing multiple new intrinsic and extrinsic toughening mechanisms. These include (a) debonding of the GNPs, (b) microcracking leading to crack deflection and branching ahead of the main crack, (c) pull-out, crack bridging and rupture of the GNPs, and (d) the formation of debris inside the advancing fatigue crack which promotes a crack tip shielding effect behind the crack front. These toughening mechanisms can operate more effectively when the GNPs are aligned normal to the direction of the advancing crack and are hindered if the GNPs form agglomerates.

4 CONCLUSIONS

In the present work we have investigated the effectiveness of electric field alignment of graphene nanoplatelets (GNPs) in increasing the fatigue resistance of epoxy nanocomposites. The GNPs were aligned in an uncured (liquid) epoxy resin by applying an alternating current electric field during the curing process, before gelation of the epoxy. The fatigue properties of the cured epoxy containing the aligned or randomly-orientated GNPs, at concentrations of 0.5, 1.0, 1.5 and 2.0 wt%, were measured using double cantilever beam (DCB) specimens tested in displacement control over a range of cyclic energy release rates from the threshold condition (i.e. where no fatigue crack growth was observed) to fast fracture being recorded.
The results showed that aligning the GNPs using an electric field yielded a greater improvement in the fatigue crack growth resistance than obtained using randomly-orientated GNPs for a given concentration, particularly in the near fatigue-threshold region. Further, the resistance of the epoxy nanocomposites to fatigue crack growth was found to increase as the concentration of the randomly-orientated or the aligned GNPs was increased up a concentration of 1.5 wt%, beyond which no further improvement in the fatigue resistance was observed due to significant agglomeration of the GNPs occurring in the epoxy at the highest concentration used of 2.0 wt%.

The presence of GNPs in the epoxy promoted an enhancement of the fatigue resistance in the epoxy nanocomposites via inducing multiple new intrinsic and extrinsic toughening mechanisms. These included (a) debonding of the GNPs, (b) microcracking leading to crack deflection and branching ahead of the main fatigue crack, (c) pull-out, crack bridging and rupture of the GNPs, and (d) the formation of debris inside the advancing fatigue crack which promoted a crack tip shielding effect behind the crack front. These toughening mechanisms operated more effectively when the GNPs were aligned normal to the direction of the advancing crack and were hindered if the GNPs formed agglomerates.

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Table 1. The quasi-static and cyclic fatigue properties of the unmodified epoxy and GNP epoxy nanocomposites.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$G_I$ (J/m²)</th>
<th>$\Delta G_{Ieq,th}$ % Increase (GNP addition)</th>
<th>$\Delta G_{Ieq,th}$ % Increase (E-Field)</th>
<th>$G_{I_{max,th}}$ (J/m²)</th>
<th>$\Delta G_{I_{eq,th}}$ % Increase (GNP addition)</th>
<th>$\Delta G_{I_{eq,th}}$ % Increase (E-Field)</th>
<th>$m$</th>
<th>$C$</th>
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</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>165</td>
<td>-</td>
<td>-</td>
<td>11</td>
<td>4.62</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.5 wt.% random</td>
<td>336</td>
<td>104%</td>
<td>-</td>
<td>41</td>
<td>16.0</td>
<td>247%</td>
<td>77%</td>
<td>2.4</td>
</tr>
<tr>
<td>0.5 wt.% aligned</td>
<td>451</td>
<td>173%</td>
<td>34%</td>
<td>98</td>
<td>28.4</td>
<td>514%</td>
<td>77%</td>
<td>2.6</td>
</tr>
<tr>
<td>1.0 wt.% random</td>
<td>1028</td>
<td>523%</td>
<td>13%</td>
<td>87</td>
<td>33.3</td>
<td>619%</td>
<td>51%</td>
<td>2.9</td>
</tr>
<tr>
<td>1.0 wt.% aligned</td>
<td>1164</td>
<td>605%</td>
<td>13%</td>
<td>139</td>
<td>50.1</td>
<td>982%</td>
<td>3.1</td>
<td>0.095</td>
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<tr>
<td>1.5 wt.% random</td>
<td>1322</td>
<td>701%</td>
<td>11%</td>
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<td>1029%</td>
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<td>-</td>
<td>191</td>
<td>75.9</td>
<td>1541%</td>
<td>3.4</td>
<td>0.030</td>
</tr>
<tr>
<td>2.0 wt.% random</td>
<td>680</td>
<td>312%</td>
<td>9.1%</td>
<td>83</td>
<td>57.7</td>
<td>1146%</td>
<td>3.5</td>
<td>0.035</td>
</tr>
<tr>
<td>2.0 wt.% aligned</td>
<td>842</td>
<td>350%</td>
<td>-</td>
<td>120</td>
<td>67.3</td>
<td>1355%</td>
<td>3.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

1. Shows the improvement in the quasi-static toughness ($G_I$) with respect to the unmodified epoxy.

2. Shows the efficacy of the electric field in increasing the quasi-static toughness ($G_I$).

3. Shows the improvement in the fatigue threshold value ($\Delta G_{I_{eq,th}}$) with respect to the unmodified epoxy.

4. Shows the efficacy of the electric field in increasing the fatigue threshold value ($\Delta G_{I_{eq,th}}$).
Figure 1. Schematic showing DCB specimen fabrication and DCB fracture and fatigue testing methodology. (a) Three-roll milling process for dispersing the GNPs in epoxy. (b) Setup with glass slides as the spacers for the specimen fabrication. (c) Schematic depicting the GNP alignment in the liquid epoxy resin using an electric field. (d) DCB specimen geometry and (e) DCB fatigue test setup.
Figure 2. Cross-sectional optical micrographs of an epoxy nanocomposite (0.5 wt% GNPs) (a) before (b) 1 minute and (c) 20 minutes after exposure to the electric field. The white arrow indicates the electric field direction. The inset photographs show the contrast binary image used for graphical analysis of the GNP orientation. (d) Histogram of normalised pixel intensity against the angle of the GNPs normal to that of the direction of the electric field for the aligned and random conditions.
Crack Growth Rate (mm/cycle) vs. $\Delta G_{eq}$ (kJ/m$^2$)

(a) 0.5 wt.% Random and Unmodified

(b) 1.0 wt.% and 1.5 wt.% Aligned

Region A, Region B, Region C
\[ \Delta G_{leq} \ (kJ/m^2) \]

(c)

\[ \Delta G_{leq} \ (kJ/m^2) \]

(d)
Figure 3. Fatigue crack growth rate curves for the unmodified epoxy and the epoxy nanocomposites containing GNP at the concentrations of (a) 0.5, (b) 1.0, (c) 1.5 and (d) 2.0 wt%. (e) All curves plotted together for comparison.
Figure 4. Cross-sectional scanning electron micrographs of the crack tip region (in Region C: high $da/dN$) of the (a) unmodified epoxy, (b) epoxy nanocomposite containing 0.5 wt% randomly-orientated GNPs and (c) epoxy nanocomposite containing 0.5 wt% of aligned GNPs. The arrows indicate microcracks caused by the GNPs and the circled region indicates the location of the main fatigue crack tip. The direction of fatigue crack growth is from left to right.
Figure 5. Scanning electron micrographs of the epoxy nanocomposite containing 0.5 wt% of random GNP’s (in Region A: low $da/dN$) of (a) the crack tip process zone (b) crack tip branching and the GNPs are marked by red arrows and (c) microcrack formation due to GNP-epoxy interfacial debonding (note that the GNPs are seen to bridge a microcrack).
**Figure 6.** Scanning electron micrograph of the fracture surface (at Region C: high $da/dN$) of an epoxy nanocomposite (0.5 wt.% of randomly-orientated GNPs) showing interfacial debonding and epoxy void growth by a pulled-out GNP particle and microcracking in the epoxy.

**Figure 7.** Scanning electron micrographs of the fatigue crack surfaces (at Region C: high $da/dN$) of the (a) unmodified epoxy and nanocomposites containing (b) 0.5 wt% and (c) 2.0 wt% of randomly-orientated GNPs. Note the increase in the surface roughness with increasing GNP concentration due to crack tip branching.
Figure 8. Cross-sectional scanning electron micrograph of epoxy nanocomposite of 0.5 wt.% aligned GNPs (at Region A: low $da/dN$) showing bridging and rupture of GNPs across the fatigue crack.

Figure 9. Scanning electron micrograph of the fatigue fracture surface (in Region C: high $da/dN$) of a nanocomposite containing 0.5 wt.% aligned GNPs showing epoxy void sites where aligned GNPs have been pulled-out of the epoxy matrix.
Figure 10. Cross-sectional scanning electron micrograph of debris particles (in Region A: low $da/dN$, in a 0.5 wt. % aligned GNP epoxy nanocomposite) along the fatigue crack which induce a crack tip shielding effect.