**Improvements to the Mode I Fatigue Resistance of Epoxy Nanocomposites Using Aligned Graphene Nanoplatelets**

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**ABSTRACT**

Improvements to the mode I fatigue resistance of epoxy nanocomposites containing randomly-orientated or aligned graphene nanoplatelets (GNPs) are examined in the present paper. The GNPs were aligned within an uncured (liquid) epoxy resin by applying an AC electric-field. Alignment of the GNPs (up to 2 wt.%) in the direction of the electric-field was retained following gelation and cure of the epoxy to create the aligned-GNP epoxy nanocomposites. The fatigue properties were measured using double cantilever beam (DCB) specimens of composite substrates bonded with the epoxy polymer as the adhesive, where the crack propagated through the adhesive layer. The epoxy polymer layer was either the unmodified epoxy or the epoxy nanocomposites containing the GNPs. The DCB specimens were tested under cyclic-fatigue loading. Experimental testing reveals an improvement to the fatigue resistance by both the addition of the randomly-oriented and the aligned GNPs, particularly when the crack growth length per load cycle is less than the GNP length (which was \(\sim 25\ \mu m\)). The fatigue resistance is improved by the GNPs promoting several toughening mechanisms which retard the crack growth rate: including microcrack and microvoid formation ahead of the crack tip, crack branching, bridging and pull-out of the GNPs, and crack shielding by debris immediately behind the crack tip. These toughening mechanisms become more active when the GNPs are aligned normal to the fatigue crack growth direction, resulting in superior fatigue resistance compared to the epoxy nanocomposites containing randomly-oriented GNPs.
1 INTRODUCTION

Fiber-reinforced polymer composites are widely used in aircraft and other light-weight structures. However, a safety concern is that brittle epoxy-matrix composite materials are susceptible to fatigue-induced delamination cracking under moderately low cyclic loads [1]. Various techniques can be used to increase the fatigue resistant properties of polymers and polymer matrix composites. The addition of nano-sized fillers to the polymer matrix, such as SiO$_2$ [2], carbon nanofibers [3], graphene nanoplatelets [4] or carbon nanotubes [5], are effective methods to improve the interlaminar fracture toughness of composite materials. The majority of studies have been performed on materials containing nano-fillers which are randomly oriented [6]. For example, Blackman et al. [7] and Hseih et al. [8] investigated the fracture toughness and fatigue properties epoxy containing randomly-oriented SiO$_2$ nanoparticles or carbon nanotubes (CNTs), respectively.

Amongst all nanofillers, graphene nanoplatelets (GNPs) are of particular interest due to their excellent mechanical and other properties [9]. Studies into the fracture toughening and fatigue toughening of polymers using graphene have only considered GNPs which are randomly oriented. The effects of random GNPs on improvements to (a) the mode I fracture toughness [10], (b) the fatigue resistance (randomly dispersed GO) [11] and (c) the flexural fatigue behaviour (randomly oriented hybrids graphene and carbon-nanofibers) have been determined [12]. However, the effect of using aligned GNPs on the interlaminar fatigue resistance of composite materials has not yet been evaluated. Investigating this area is important, as fatigue loading is a common cause of damage to aircraft structures and engine components made of composite materials [13].

In the present paper an experimental study into the alignment of GNPs in epoxy composites using an external AC electric-field is described. Particularly, the determination of the effect of this alignment on the mode I interlaminar fracture and fatigue behaviour are considered. An unmodified epoxy polymer (i.e. without any GNPs) and epoxy-polymer nanocomposites containing different concentrations of GNPs (i.e. 0.5, 1.0, 1.5 & 2.0 wt.%), which are randomly oriented or aligned using an electric-field, are fatigue tested over a range of cyclic strain-energy release-rates. The fatigue toughening mechanisms induced by the GNPs in the random and aligned conditions are also determined. Using this approach, the optimum alignment and content of GNPs can be identified to provide improved fatigue-resistant epoxy materials.

2 MATERIALS AND METHODS

2.1 Fabrication of Nanocomposites and Electric-field Alignment

The process used to manufacture the nanocomposite specimens 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 m$^2$/gm were used [14]. The GNPs were mixed into a liquid epoxy consisting of a blend of Bisphenol A and Bisphenol F (West System). GNPs were added in appropriate amount to achieve the intended concentration in a solution which included both the resin and the hardener. GNPs with different concentrations (i.e. 0.5, 1.0, 1.5 & 2.0 wt.%) were initially manually mixed in the resin, which was then passed through a three-roll mill (Dermamil 100) to obtain a good dispersion (Fig. 1a). The 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 modified aliphatic polyamine (206, West System), was mixed into the epoxy resin at a weight ratio of 1:5.36.
Carbon-fibre epoxy-matrix (CFRP) composite substrates were employed as the substrates which were fabricated using 12 plies of unidirectional T700 (24K) prepreg (VTM264 supplied by Cytec Industrial Materials). The composite was cured and consolidated in an autoclave at 120°C at 620 kPa (90 psi) for one hour, which are the process conditions recommended by the prepreg manufacturer. After curing, the surfaces of the composite were sand-blasted using glass beads as the abrasive media to promote surface roughness to aid subsequent adhesive bonding with the epoxy nanocomposites. Following sand-blasting, any surface contamination was removed using acetone.

The double cantilever beam (DCB) specimens were made consisting of a 3 mm thick epoxy layer (with or without GNPs) sandwiched between two 0.5 mm thick composite substrates. The thickness of the nanocomposite layer was accurately controlled using glass slides as spacers (Fig. 1b). A Teflon film (50 mm long × 50 µm thick) was located at the mid-thickness of the epoxy-based layer before curing, and this was used as the initiation point for fatigue cracking during testing. To align the GNPs in the through-thickness direction, the CFRP composite substrates were used as the electrodes (Fig. 1c). A sinusoidal AC electric-field with a strength of 25 V/mm and frequency of 10 kHz was generated between the two composite substrates using a Tektronix CFG250 generator whose signal was amplified using a Krohnite 7602M amplifier. The electrical-field was applied to the initially uncured 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, i.e. the cured) condition. The GNPs were initially randomly oriented but rotated and aligned in the direction of the electric-field while suspended in the liquid epoxy, as shown in Figure 2. The GNPs joined together end-to-end to form chain-like structures which extended between the composite substrate electrodes. This state was retained as the epoxy underwent gelation and curing, thereby locking in the aligned structure of the GNPs (Fig. 2b).

The epoxy formulations were cured at room temperature for 72 h. The as-prepared composites were cut using a diamond saw into DCB test specimens which were 230 mm long × 20 mm wide × 4 mm thick (Fig. 1d). At least five DCB tests were performed on the unmodified epoxy and the epoxy nanocomposites with different GNP contents (Fig. 1e).
Figure 1. Schematic depicting specimen fabrication and testing methodology. a. Three-roll milling for dispersing the GNPs in epoxy; b. Setup with glass slides as the spacers for the specimen fabrication; c. Schematic depicting the GNP alignment by the electric-field; d. and e. the DCB specimen and the DCB fatigue test setup, respectively.

Figure 2. Cross-sectional micrographs of an epoxy nanocomposite (0.5 wt% GNPs) under an external AC electric-field at times of a. 1 minute and b. 20 minutes. The white arrow indicates the electric-field direction.

2.2 Fracture Toughness and Fatigue Testing

The mode I fracture toughnesses of the unmodified epoxy and epoxy nanocomposites were determined using the DCB test in accordance with ISO 25217:2009 [15]. 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 (an ‘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 arrest the 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 this data, the mode I strain energy release rate ($G_{IC}$) was calculated using corrected beam theory:

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

(1)
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.

Mode I fatigue testing of the materials followed ASTM D6115 specifications [16]. The pre-cracked end of the DCB specimens were tested in displacement control by applying a cyclic crack opening-crack closing condition using a 3 kN fatigue testing machine (an ‘Instron E-3000’). The load was applied using a sinusoidal waveform at a cyclic frequency of 5 Hz. The $R$-ratio was 0.5, which defines the ratio between the minimum and maximum crack opening displacements applied in a single load cycle. The fatigue crack was grown over a short length (typically 0.9 mm-1.2 mm) under a constant fatigue load condition, and from this the cyclic strain energy release rate was calculated using:

$$G_{I_{max}} = \frac{3P_{max}\delta_{max}}{2b(a + |\Delta l|)}$$

$P_{max}$ is the maximum load and $\delta_{max}$ is the maximum displacement in a single load cycle. The magnitude of $G_{I_{max}}$ decreased as the fatigue crack propagated along the DCB specimen, which enabled its relationship with the fatigue crack growth rate per cycle ($da/dN$) to be determined.

3 RESULTS AND DISCUSSION

3.1 MODE I FRACTURE TOUGHNESS

$G_{Ic}$ values obtained for the 3 mm thick epoxy nanocomposite 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. When compared to the unmodified epoxy polymers, the value of $G_{Ic}$ increases from 0.165 kJ/m² to 0.336 kJ/m² for a nanocomposite containing 0.5 wt.% of GNPs; which represents an approximately two times increase. In comparison, alignment of the GNPs for the same concentration registers an increase of about three times ($G_{Ic}$ of 0.451 kJ/m²) compared to the unmodified epoxy polymer. 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. A maximum absolute increase of about nine times is recorded 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.

3.2 MODE I FATIGUE RESISTANCE

Fatigue crack growth rate curves are presented in Figure 3 which show plots of the fatigue crack growth rate per cycle versus the maximum cyclic strain-energy release-rate for the unmodified epoxy and the epoxy nanocomposites containing different concentrations of the randomly-oriented or aligned GNPs. The fatigue property values for these materials are given in Table 1. The curve fit in the figure was obtained using the technique described in [17]. As for the static fracture toughness values, the addition of randomly-oriented GNPs to the epoxy improves their fatigue behaviour. For example, the crack growth rate is retarded and the value of $G_{max\_th}$ increases, where $G_{max\_th}$ is the threshold value of the cyclic energy release rate below which no fatigue crack growth will occur. The value of $G_{max\_th}$
increases rapidly with the concentration of randomly-oriented GNPs up to 1.5 wt%, where a times eleven increase is achieved, compared to the unmodified epoxy polymer. Other studies have also measured improvements in the $G_{\text{max},\text{th}}$ value of polymers by the addition of randomly-oriented nanoparticles, including SiO$_2$ nanoparticles [7], CNTs [8] and graphene oxide [11]. The gradient of the crack growth rate curve, defined by the parameter $m$, increases with the concentration of randomly-oriented GNPs. This gradient defines the sensitivity of a material to fatigue-induced crack growth in the linear portion of the crack growth rate curve, and the rising $m$ value with GNP content is indicative of the decreasing fatigue resistance of the epoxy nanocomposite. In summary, the crack growth rate curves show that the fatigue resistant properties of the epoxy increase with the concentration of GNPs, although they are most effective in the near threshold region when the crack growth rates are low (i.e. under $\sim 10^{-4}$ mm/cycle).

Electric-field alignment of the GNPs normal to the crack growth direction further improved the fatigue resistance of the epoxy nanocomposites. Compared to the epoxy nanocomposite containing randomly-oriented GNPs, aligning the GNPs provided the greatest improvements in the fatigue resistance at relatively slow crack growth rates when the cyclic crack opening values were small (Figure 3: Regime A). The critical strain energy release rate values for crack initiation were higher when the GNPs were aligned rather than randomly-orientated. Apart from the high GNP content nanocomposites when agglomeration occurred, the $G_{\text{max},\text{th}}$ value is increased by $\sim 0.055$ kJ/m$^2$ by aligning the GNPs in the epoxy nanocomposites alignment (see Table 1). However, the improvement in the fatigue resistance by aligning the GNPs became progressively less (compared to the random GNPs) when the cyclic strain-energy release-rate was increased. This effect is observed for the different concentrations of GNP studied, except for the highest content when no significant difference was found between the randomly-orientated and aligned GNPs. This is most clearly observed in the enlarged section of the crack growth rate curves for the 0.5 wt% content, with the fatigue crack growth rates for the nanocomposite containing aligned GNPs being only slightly slower than for the nanocomposite containing randomly-orientated GNPs in Regime B, which equates to crack growth rate values in the range of $\sim 5 \times 10^{-4}$ (0.5 µm) to $5 \times 10^{-2}$ (50 µm) mm/cycle. In this regime the rate of incremental crack growth reaches, and begins to exceed, the length of the GNPs, which had an average platelet diameter of $\sim 25$ µm, with agglomeration possibly further increasing the mean size.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$G_C$ (kJ/m$^2$)</th>
<th>$G_{\text{max,th}}$ (kJ/m$^2$)</th>
<th>$G_{\text{max,th}}$ Increase (GNP addition)</th>
<th>$G_{\text{max,th}}$ Increase (E-Field Application)</th>
<th>Crack growth rate Curve Gradient (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>0.165</td>
<td>0.011</td>
<td>-</td>
<td>-</td>
<td>1.70</td>
</tr>
<tr>
<td>0.5 wt.% random</td>
<td>0.336</td>
<td>0.041</td>
<td>45 %</td>
<td>-</td>
<td>1.70</td>
</tr>
<tr>
<td>0.5 wt.% aligned</td>
<td>0.451</td>
<td>0.098</td>
<td>791 %</td>
<td>513 %</td>
<td>2.121</td>
</tr>
<tr>
<td>1.0 wt.% random</td>
<td>1.028</td>
<td>0.087</td>
<td>691 %</td>
<td>60 %</td>
<td>2.50</td>
</tr>
<tr>
<td>1.0 wt.% aligned</td>
<td>1.164</td>
<td>0.139</td>
<td>1164 %</td>
<td>60 %</td>
<td>2.90</td>
</tr>
<tr>
<td>1.5 wt.% random</td>
<td>1.322</td>
<td>0.133</td>
<td>1109 %</td>
<td>44 %</td>
<td>1.387 (1.223 to 1.552)</td>
</tr>
<tr>
<td>1.5 wt.% aligned</td>
<td>1.473</td>
<td>0.191</td>
<td>1635 %</td>
<td>44 %</td>
<td>2.50</td>
</tr>
<tr>
<td>2.0 wt.% random</td>
<td>0.680</td>
<td>0.083</td>
<td>655 %</td>
<td>-</td>
<td>3.852</td>
</tr>
<tr>
<td>2.0 wt.% aligned</td>
<td>0.842</td>
<td>0.12</td>
<td>991 %</td>
<td>45%</td>
<td>3.960</td>
</tr>
</tbody>
</table>
Fractographic examination of the DCB specimens during, and following, testing revealed that the GNPs induced multiple fatigue toughening mechanisms which increased the fatigue resistant properties of the epoxy. Both intrinsic and extrinsic mechanisms were operative, including those dependent on the crack tip opening displacement (CTOD). They are summarised in Table 2. Examples of some of these fatigue toughening mechanisms are shown in Figure 4. Ahead of the main crack tip, the intrinsic mechanisms were nanoparticle/epoxy debonding leading to microcracking, localised plastic yielding leading to void formation adjoining the GNPs, and crack deflection and branching leading to a tortuous crack path.
Figure 4: SEM micrographs showing fatigue toughening mechanism acting ahead of the crack-tip. (a1, a2, a3) Cross-sectional images showing increasing crack branching with increasing GNP content, (b1,b2,b3) Fracture surface images showing increasing roughness due to crack branching with increasing GNP content. (c) Shows plastic yield of the matrix around the GNPs leading to void formation (d) Fracture surface showing sites where GNPs have been pull-out. (e) GNP-epoxy debonding sites leading to micro-cracking.

Behind the crack tip, the extrinsic mechanisms were crack bridging and pull-out by the GNPs and crack tip shielding by debris particles. Figure 5.a and 5.b show an SEM micrograph and a schematic of wedging/microbuckling of GNPs along the crack. Figure 5.c and 5.d shows debris particles wedged between the crack surfaces, which are formed by fragments of the epoxy nanocomposite breaking away from the bulk material due to the extensive branching at the crack tip caused by the GNPs. This induces physical contact between the mating crack surfaces as the value of $G_{\text{min}}$ is approached. These mechanisms lower the cyclic strain intensity (specifically $\sigma_{\text{min}}$) exerted on the crack tip, and thereby retard the rate of fatigue crack growth.
Table 2: Mechanisms sensitive to orientation of the nanoparticles and the crack tip opening displacement (CTOD).

<table>
<thead>
<tr>
<th>Applicable Toughening Mechanisms</th>
<th>Orientation Sensitive</th>
<th>CTOD Sensitive</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intrinsic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crack Deflection</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>Crack Branching</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>Microcrack formation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Matrix Voiding/Plastic Deformation</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Extrinsic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Debris or Nanoparticle induced</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Wedging/Microbuckling</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roughness Induced Crack Closure</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>Toughening</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Bridging</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pull-out</td>
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</table>

**Figure 5**: SEM micrographs (a,c) showing extrinsic fatigue strengthening mechanisms (Microbuckling and matrix debris induced toughening). These mechanisms contribute significantly near the threshold (where the CTOD is small) (b,d). Show corresponding schematics a. Microbuckling/wedging of GNP. b. Corresponding schematic highlighting microbuckling of quasi aligned/aligned platelets at low CTOD. c. Matrix debris due to GNP particles wedged along the crack. d. Schematically shows that such asperities enhance toughness at low CTOD.

**4 CONCLUSIONS**

Previous research has demonstrated improvements to the fracture and fatigue resistance of epoxy polymer nanocomposites using randomly-oriented nanoparticles of silica, rubber or carbon (e.g. nanofibres, CNTs, graphene). This study has demonstrated that the addition of randomly-oriented GNPs to the epoxy polymer also improves their fracture and fatigue behaviour. Most importantly, below a GNP concentration of 2 wt. %, the electric-field alignment of GNPs before curing of the epoxy nanocomposites is a very effective method for further increasing their fracture and fatigue
resistance. Indeed, the improvements in the fatigue resistance, particularly at low cyclic strain-energy release-rates near the threshold value below which no fatigue crack growth occurs, was significantly enhanced by the electric-field alignment of the GNPs. The fatigue resistance of the epoxy nanocomposites was improved via multiple intrinsic and extrinsic fatigue toughening mechanisms, including nanoparticle/epoxy debonding, microcracking, crack deflection/branching, and localised plastic yielding leading to void formation adjoining the GNPs ahead of the crack front. Further, behind the crack tip the extrinsic toughening mechanisms were crack bridging and pull-out by the GNPs, and crack shielding by debris particles. Thus, the electric-field alignment of the GNPs amplifies several of these toughening mechanisms, particularly in the near-threshold region (crack branching, crack bridging and pull-out, crack shielding) resulting in superior fatigue resistance. Therefore, using this approach, the optimum alignment and content of GNPs can be identified to provide improved fatigue-resistant epoxy polymer materials.

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