EPOXY NANOCOMPOSITES WITH ALIGNED CARBON NANOFLILERS BY EXTERNAL ELECTRIC FIELDS

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ABSTRACT

This paper presents systematic studies on aligning carbon nanofillers in epoxy by external fields, either electric fields or magnetic fields, to create nanocomposites with greatly improved mechanical and electrical properties. Carbon nanofibers (CNFs) and graphene nanoplatelets (GnPs) were observed to align along the field direction in the epoxy resin. Compared to the unmodified epoxy and those with randomly-oriented carbon nanofillers, the nanocomposites with aligned carbon nanofillers showed significantly higher fracture toughness and electrical conductivity along the direction of the external field. Compared with randomly-oriented nanofillers, aligned GnPs and CNFs produced 40% and 27% improvement in fracture energy at 1.0 wt%, bringing the total increase in fracture energy over the neat polymer to more than 10 times. Several key toughening mechanisms were identified through fractographic analysis, which was used to develop predictive models to quantify the increases in the value of $G_{ic}$ as a result of 1-D and 2D carbon nanofillers. The present findings suggest that aligning carbon nanofillers presents a very promising technique to create multi-scale reinforcement with greatly increased electric conductivity and fracture toughness.
1 INTRODUCTION

Advanced light-weight, high-strength fiber-reinforced epoxy composites represent a fast growing industry that is vital to the economic future. However, the low through-thickness strength and toughness makes them susceptible to matrix cracking, interfacial debonding, fibre breakage and delamination [1], which largely limits its broad applications. Moreover, the low through-thickness electric conductivity, which is dominated by the dielectric matrix phase, makes composite structures vulnerable to lightning strikes and electrostatic accumulation [2]. Therefore, it is of significant importance to improve the multifunctional properties of fiber-reinforced composites in the thickness direction.

Carbon nanofillers such as graphene nanoplatelettes (GnPs), carbon nanofibers (CNFs), and carbon nanotubes (CNTs) are promising nanofillers for composite materials [3–5]. The incorporation of carbon nanofillers can provide composites with multifunctionality and greatly improved mechanical properties. For instance, Hubert et al. [3] reported significant improvement in fracture toughness (48% and 143% increase in Mode I and Mode II fracture energy) by adding multiwall carbon nanotubes to carbon fiber laminated composites. Ruoff et al. [4] developed graphene based polymer nanocomposites showing an electric percolation threshold as low as ~ 0.1 vol%.

The full potential of such carbon nanomaterials as reinforcements has been limited because of the difficulties associated with poor dispersion and interfacial interactions between nanofillers and polymer matrix, and particularly, the controlled orientation of nanofillers [6–9]. Electric field has been reported as a promising technique to align carbon nanotubes in liquid resin. Extremely low electrical percolation threshold at approximately 0.0031 vol% was achieved by aligning CNTs, which was one order of magnitude lower than the nanocomposites with randomly oriented CNTs [7]. In our recent studies, we reported additional improvement in electrical and mechanical properties of epoxy nanocomposite by aligning carbon nanofibers using electric field [10] and magnetic field [11]. However, to the authors’ knowledge, no detailed comparative studies have been reported on the effects of aligning carbon nanofillers (carbon nanofiber or graphene) on the electric and mechanical properties of nano-composites.

This present focuses on the alignment of graphene nanoplatelettes (GnPs) and carbon nanofibers (CNFs) in epoxy by an external electric field or magnetic field and its effects on the fracture toughness and electric conductivity of the resulting nanocomposites. The fracture energy of epoxy reinforced with various contents of CNFs or GnPs was measured using mode I double cantilever beam specimens. Alternating current electric field or magnetic field normal to the bond surface was applied during the curing of the resin. Mode I fracture energy and electrical conductivity are compared with those pertinent to the unmodified epoxy.

2 EXPERIMENTAL

2.1 Materials

Vapour grown carbon nanofibres (Pyrograf®-III, grade PR-24-XT-HHT) were used in the present work. The CNFs have an average diameter of 100 nm and a length of 50–300 µm, according to the supplier. The graphene nanoplatelettes (GnPs) used in this study were obtained from XG Science, with an average thickness of approximately 6 to 8 nanometers and an average diameter of 25 µm. The epoxy resin (105) and slow hardener (206) were both supplied by WEST SYSTEM®. Composite laminates were manufactured from 12 plies of T700 carbon fibre/epoxy unidirectional prepreg (VTM 264) supplied by Applied Composites Group. The laminates, measuring 300 mm × 250 mm × 2.65 mm, were cured in an autoclave at 120 °C for 1h as recommended by the manufacturer.

2.2 Specimens and Testing methods

Double cantilever bending (DCB) specimens were manufacturing by placing the epoxy, with and without nanofillers, between two composite laminates. A Teflon coated tape about 0.11 mm thick is used as a crack starter. The bonded joint configuration was designed to simulate the high level of constraint experienced by interlaminar cracks in a composite laminate. The thickness of the adhesive layer was kept at 2 mm. An AC electric field of 25 V/mm at 10 kHz was applied, using the conductive
carbon fibre laminates as electrodes, between the adherends during the initial 1 hour period of the curing while the epoxy resin remained liquid. DCB specimens were tested in a 10 kN Instron machine at a crosshead speed of 1 mm/min in accordance with ISO 25217. The fracture energy, $G_f$, was calculated based on corrected beam theory.

3 RESULTS AND DISCUSSION

3.1 Improvements in electrical conductivity

The responses of the GnPs and CNFs to the AC electric field were investigated by optical microscopy. Initially, both GnPs and CNFs were dispersed using three role mill to be randomly oriented in the epoxy resin as shown in Fig. 1a and 1c. Upon the application of the electric field, the GnPs and CNFs started to align along the direction of the electric field. After applying the electric field for approximately 20 minutes, chain-like networks were observed (see Fig. 1b and 1d).

![Image](https://via.placeholder.com/150)

Figure 1: Optical micrographs of the epoxy nanocomposites with (a) randomly oriented GnPs, (b) aligned GnPs, (c) randomly oriented CNFs, and (d) aligned CNFs.

When subjected to an electric field, GnPs and CNFs are polarized due to the different dielectric properties and electrical conductivity from that of the liquid medium (epoxy) [12]. In addition, both GnPs and CNFs are shape anisotropic, causing a torque that drives GnPs and CNFs to rotate to the direction of the electric field. Due to the presence of opposite charges at the ends, the aligned nanofillers attract each other to form chain-like structure as shown in the Figure 1b and 1d.

Fig. 2 show the effects of GnPs and CNFs content and alignment on the electrical conductivity of the respective epoxy composites. The electrical conductivity increased with the content of carbon nanofillers regardless of the orientation. The composite with aligned carbon nanofillers showed consistently higher electrical conductivity. For instance, the epoxy nanocomposites with 0.5 and 1.0 wt% of aligned GnPs showed nearly three orders of magnitude higher conductivity than the corresponding nanocomposites with the same content of randomly oriented GnPs. The results clearly show that aligning carbon nanofillers increases the electrical conductivity of epoxy more than when they are randomly oriented. The electric field induced directional alignment and end-to-end connection
of the carbon nanofillers facilitate the formation of conductive path for electrons resulting in improved electrical conductivity.

3.2 Improvements in fracture toughness

Fig. 3 shows the $G_{\text{IC}}$ of epoxy nanocomposites with different contents of randomly oriented and aligned GnPs and CNFs. The critical fracture energy increased significantly with the addition of carbon nanofillers. The unmodified epoxy showed $G_{\text{IC}}$ of ~134 J/m², which increased to ~1072 J/m² with the addition of 2.0 wt% of randomly-oriented GnPs. The application of an electric field further improved the fracture toughness. For example, the epoxy nanocomposites with 0.5 and 1.0 wt% of aligned GnPs showed ~40% improvement compared with those with randomly-oriented GnPs. However, at higher GnP wt% the increase in fracture energy due to alignment is only marginal. For epoxy/CNFs nanocomposites, the addition of 1.0 wt% of CNFs with random orientation yielded up to nearly 10 times improvement in $G_{\text{IC}}$. With alignment, the total fracture energy reached 12 times that of
unmodified epoxy. This demonstrates that extraordinarily high toughening efficiency was obtained by the electric field-induced alignment.

The fracture was observed to be cohesive through the nanocomposite adhesive layer. As shown in Fig. 4, SEM micrograph of the fracture surface revealed a significant number of CNFs and GnPs undergoing debonding and pull-out from the epoxy matrix. In addition, some of the nanofillers showed the presence of distinct voids around the debonded nanofillers (see Fig. 4b and 4d), which are indicative of the plastic void growth in epoxy. The epoxy void growth and the nanofiller pull-out as well as debonding dissipate energy during fracture process resulting in improved toughness of the epoxy nanocomposites. In most fibrous composites, the fibre pull-out is considered to be the dominant toughening process which is included in the numerical toughening model in the following section.

![Figure 4](image)

Figure 4: SEM micrograph of the nanofiller modified epoxy nanocomposite fracture surface; (a) and (b) GnP/epoxy nanocomposite; (c) and (d) CNF/epoxy nanocomposite.

3.5 Modelling of the nanocomposite toughness

A generalized toughness theory proposed by Hsieh et al [17] is adopted here to quantify the observed increase in fracture energy due to alignment. The total fracture energy is given by the sum of the separate contributions from nanofiller pull-out ($G_{po}$), debonding ($G_{db}$) and the epoxy void growth ($G_{vd}$) mechanisms. The toughening due to filler pull-out is attributed to the frictional work in pulling the filler out of the matrix. The pull-out theory of Cottrell and Kelly [13,14] expressed the toughness due to pull-out as follows:

$$
\Delta G_{po,CNF} = n \frac{\nu \sigma_k \ell_k}{12} = n \frac{\nu \sigma_f^2 d}{24 \tau}
$$

(1)
where $l_c = \sigma_d/2\tau$ is the critical transfer length of the nanofiller, and $n$ denotes an orientation efficiency factor. Similarly, the expression for pull-out of a two-dimensional nano-sheet (i.e. GnP) can be derived using the approach outlined by Hull [15] as follows:

$$\Delta G_{\text{po, GnP}} = n\frac{n v_f \sigma_d t}{24\tau}$$

(2)

The associated parameters are defined in Table 1. Since Eq. (1) is originally derived for composites with aligned fillers, the effective volume fraction of reinforcement filler participating in the pull-out toughening mechanism is less than the nominal $v_f$. Assuming a uniform probability of fibre orientation in three dimensions, Romualdi and Mandel have shown that the orientation efficiency factor $n$ is $2/\pi$ [16]. Further numerical [17] and experimental [18] work have later confirmed the orientation efficiency factor to be about 0.55 depending on the degree of randomness.

In addition to the CNF pull-out mechanism, the plastic void growth of epoxy matrix promoted by debonding of CNFs from the epoxy matrix would further improve the fracture toughness. This arises because in the process zone ahead of the crack tip, where a triaxial stress-field exists, the nanofillers debond from the epoxy as the local stresses rise as the applied load is increased. The debonded nanofiller act as voids in the epoxy, allowing the polymer to deform plastically, which in turn increase the void size. A 30 percent increase in the size of the voids around the debonded nanofiller was found in most cases. In previous studies [19,20], the plastic void growth mechanism was quantitatively shown to significantly improve the fracture toughness of nanofiller modified epoxy. Huang and Kinloch [21] have shown that the fracture energy contribution from the plastic void growth mechanism can be calculated as follows:

$$\Delta G_v = \left(1 + \frac{\mu v_f}{\sqrt{\pi}}\right)^2 (v_f v_t - v_t)\sigma_d r_{yu} K^2$$

(3)

The plastic zone size ($r_{yu}$) at the fracture energy of the unmodified epoxy ($G_{cu}$) is given by:

$$r_{yu} = \frac{1}{6\pi} \frac{E_m G_{cu}}{(1-v^2)\sigma_d^2}$$

(3)

Therefore the fracture energy of the nanofiller toughened epoxy is given as:

$$G_{\text{Nano}} = G_{CU} + \Delta G_{\text{po}} + \Delta G_v$$

(4)

The values used to calculate the fracture energy of the epoxy polymers containing nanofillers are given in Table 1. Fig. 5 shows a comparison of the analytical modelling results with the experimental values, where the orientation efficiency factor $n$ is taken to be 0.55. The model shows a good correlation with the experimental results predicting similar fracture energy improvements.

![Figure 5: Comparison of the experimental fracture energy results for the nanofiller modified epoxy with the analytical modelling studies; (a) GnP/epoxy nanocomposites and (b) CNF/epoxy](image)
Table 1: Values of the parameters in the analytical model of nanocomposites.

<table>
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<tr>
<th>Parameter</th>
<th>Symbol</th>
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<th>Value</th>
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<td>[22]</td>
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<tr>
<td>GnP thickness</td>
<td>$t$</td>
<td>nm</td>
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<td>[23]</td>
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<td>kg/m$^3$</td>
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<td>kg/m$^3$</td>
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<tr>
<td>Density of unmodified epoxy</td>
<td>$\rho_m$</td>
<td>kg/m$^3$</td>
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<td>[25]</td>
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<tr>
<td>Nanofiller/epoxy interface shear strength</td>
<td>$\tau$</td>
<td>MPa</td>
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<tr>
<td>CNF/epoxy interface fracture energy</td>
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<td>J/m$^2$</td>
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<td>[24]</td>
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<tr>
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<td>[23]</td>
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9 CONCLUSIONS

Epoxy nanocomposites with aligned GnPs and CNFs have developed by using external electric fields. Based on the optical microscopy investigation, the majority of carbon nanofillers have been successfully re-oriented along the external field direction. The alignment of carbon nanofillers significantly increases the electrical conductivity as well as the fracture toughness of the epoxy. The main toughening mechanisms have identified through fractographic analysis. By quantifying the contributions by these mechanisms, an analytical model has been successfully developed and shown to correctly account for the increase in fracture energy by 1-D and 2D carbon nanofillers. This work demonstrates that carbon nanofillers can be manipulated by external electric field to achieve high level of alignment, thus enabling the fabrication of high-performance multifunctional epoxy nanocomposites.

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