Aligning multilayer graphene flakes with an external electric field to improve multifunctional properties of epoxy nanocomposites

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1. Introduction

Improving the structural and functional properties of polymers and polymeric composites has been recognised as a key to dramatically increase their wide applications. Graphene shows great promise as a nanofiller in polymer composites due to its high physical aspect ratio, high strength and Young’s modulus, and excellent thermal and electrical conductivities [1]. Substantial property improvements can be achieved using various graphene-based materials, such as graphene oxide (GO) [2,3], thermally expanded or reduced graphene [4,5], graphene foam [6], non-covalently functionalized graphene flakes [7] etc., even when such materials are used at low concentrations in the polymer. For instance, Stankovich et al. showed that by using graphene at a volume content as low as ~0.1 vol% an electrical percolation threshold could be reached within polystyrene [2]. Rafiee et al. showed that thermally exfoliated graphite oxide provided 53% additional increase in the mode I fracture toughness of an epoxy nanocomposite compared to single- or multi-walled carbon nanotubes [3]. Song et al. recently developed epoxy/graphene nanocomposites with remarkably enhanced thermal conductivities (e.g. 1.53 W/mK) using 10 wt% of 1-pyrenebutyric acid functionalized graphene flakes [7].

However, the property improvements achieved so far using such carbon nanofillers are still much lower than the theoretical predictions because a variety of factors have not yet been optimised. Such factors include the degree of dispersion and exfoliation, and critically, the orientation of the nanoplatelets [8]. Different approaches have been reported for orienting carbon nanofillers, based mainly on employing mechanical stretching [9], an electric field [10–15], and a magnetic field [16–18]. The use of an electric field has been reported to align carbon nanotubes [10,11], carbon nanofibers [12,13], and carbon black [14] to improve the electrical conductivity and mechanical properties of polymer nanocomposites. Recently, Kim et al. developed epoxy
nanocomposites with graphite aligned along the alternating-current (AC) electric field direction and found that these materials had anisotropic tensile modulus and strength [19,20]. Chen et al. prepared polyester resin nanocomposites with graphite nanosheets oriented along the applied AC electric field, and found that the electrical conductivity was greatly increased in the alignment direction [21–23]. In spite of these studies, very limited research has been reported on the mechanisms of aligning graphene nanoplatelets (GnPs) in polymers under an external electric field and its efficiency in improving the fracture toughness, as well as the electrical and thermal properties of the resultant nanocomposites.

Epoxy thermosets represent an important class of polymers due to their versatility and are widely used as coatings, electric encapsulates, fiber-optic sheathing, adhesives and matrices for fiber-reinforced composites, etc. However, their high degree of crosslinking makes them intrinsically brittle and prone to damage, thus holding back their increased application in aerospace, automotive and advanced electric applications [24]. Moreover, their extremely low thermal and electrical conductivities greatly limit their applications that demand good dissipation of heat and static electricity [6,7]. Furthermore, the low through-thickness electrical conductivity of fiber-reinforced epoxy composites, which is dominated by the polymeric matrix phase, makes such composite structures vulnerable to lightning strikes and unable to prevent electrostatic accumulation [25]. The low electrical conductivity also hinders the diagnosis of damage by electrical-based techniques, such as the eddy-current technique. Therefore, improving the electrical conductivity, thermal conductivity and fracture toughness of epoxy polymers is of major practical importance.

The present paper describes a technique to align GnPs in an epoxy by applying an AC electric field and focuses on experimental and theoretical investigations of the effects on alignment on the electrical and thermal conductivities, and fracture toughness of the epoxy nanocomposites. To the best of our knowledge, there is no report on (a) the mechanisms controlling the alignment of GnPs in an epoxy by an AC electric field and (b) the effects of alignment on the electrical and thermal conductivity, and fracture toughness of the resulting epoxy nanocomposites. The nanoplatelets used have a carbon-to-oxygen atomic ratio of 98-to-7 and an average thickness of approximately 6–8 nm. Firstly, the electromechanical mechanisms controlling the formation GnPs are investigated. Then, the improvements arising from the GnPs (both aligned and randomly-oriented) of different volume contents in the properties of the epoxy polymer are measured and compared. Finally, the mechanisms by which the GnPs improve these properties are investigated.

2. Experimental

2.1. Materials

The GnPs used in the present study were obtained from XG Science, having an average thickness of approximately 6–8 nm and an average particle diameter of 25 µm. The C:O ratio was determined to be 93:7 by using X-ray photoelectron spectroscopy (XPS) performed employing a Thermo K-alpha XPS instrument. The liquid epoxy resin (‘105’ and hardener (‘206’) were supplied by WEST SYSTEM®. The liquid epoxy resin used was a blend of bisphenol A and bisphenol F. The liquid hardener employed was a blend of aliphatic and aliphatic amine adducts based upon diethylenetriamine and triethylenetetramine. The carbon-fibre epoxy composite substrates were manufactured from T700 carbon-fibre/epoxy prepreg (‘VTM 264’) supplied by Applied Composites Group. Twelve plies of this unidirectional prepreg, with dimensions of 300 mm × 250 mm × 2.65 mm, were used to fabricate the substrates by curing in an autoclave at 120 ºC and an overpressure of 98 kPa for 1 h.

2.2. Bulk epoxy nanocomposites fabrication

Epoxy nanocomposites with contents of 0.27, 0.54, 0.81, and 1.08 vol% of GnPs were fabricated by combining sonication and calendaring processes. The GnPs was first mixed with the liquid epoxy resin using a Hiedscher UP2005 ultrasonic homogenizer (operated at 0.5 cycles and 50% amplitude) for 30 min, which broke-up the graphene agglomerates. The mixture was then further processed by a three-roll mill (Derma mill 100) ten times at 150 rpm with a roller-gap distance of 20 µm. After this dispersion process, a stochiometric amount of hardener was added. This mixture was then degassed and poured into a custom-made silicon rubber mold. The GnPs were aligned by using an AC electric field (25 V/mm at 10 kHz) supplied by an AC signal generator (Tektronix CFG230) in combination with a wideband amplifier (Krohnhite 7602 M). Two aluminum plates were used as the electrodes and a spacer was placed between them to prepare samples of required dimensions for the various tests. Fig. S1a in Supporting information illustrates the experimental apparatus for aligning the GnPs in the epoxy resin/GnPs/hardener mixture during curing.

2.3. Double-cantilever beam (DCB) specimen fabrication

The surfaces of the carbon-fibre epoxy composite substrates used for the DCB samples were grit-blasted and thoroughly degreased with acetone to promote strong bonding with the unmodified epoxy and the epoxy nanocomposites. A dam made of silicon rubber was placed between the two substrates to prevent the liquid epoxy resin mixtures from flowing out. Spacers (2 mm thick) made of two glass slides were placed between the substrates to control the bond-line thickness. A sharp pre-crack at the mid-plane of the epoxy layer was created using a 'Teflon' film (50 µm thick) placed between the two glass slides. The epoxy/GnPs/hardener mixtures were prepared following the procedure described above and then poured between the substrates. To align the GnPs in the through-thickness direction of the epoxy layer (i.e. transverse to the subsequent direction of crack growth), the carbon fibre-epoxy composite substrates (which are electrically conductive) were used as the electrodes. An AC electric field of 25 V/mm at 10 kHz was applied between the substrates during the initial one hour of curing at room temperature. The epoxy layer was further cured at room temperature (25 ºC) for 48 h.

To prepare DCB specimens with the GnPs aligned parallel to the subsequent crack growth direction, bulk epoxy/GnPs nanocomposites (2 mm thick) were prepared following the procedures given in Section 2.2, but with the AC electric field applied across the width of the nanocomposite. These nanocomposites were then adhesively-bonded to the carbon-fibre epoxy composite substrates using an aerospace adhesive (Huntsman Araldite® 420 A/B). During the DCB fracture tests, the crack propagated in the epoxy nanocomposite layer, parallel to the alignment direction of the GnPs.

2.4. Investigation on the alignment of the GnPs

A Leica optical microscope was used to observe the response of the GnPs in the liquid epoxy resin to the AC electric field. A liquid epoxy resin/GnPs mixture, containing 0.054 vol% of GnPs, was placed on to a glass slide. Two parallel aluminum tapes were used as the electrodes to apply the AC electric field. The time-lapse images were acquired using a Leica DC 300 digital camera.
Furthermore, the orientation of the GnPs in the (cured) epoxy nanocomposites was investigated using a JEOL JEM 1010 transmission electron microscope (TEM) operated at 100 kV. TEM samples were prepared by cutting the epoxy nanocomposites into ultrathin sections of ~70 nm thick with a diamond knife using a Leica EM ultramicrotome. Scanning electron microscopy (SEM) analysis was performed using a FEI Nova NanoSEM operated at 15 kV and 5 mm working distance. For the SEM studies, the specimens were cryogenically fractured in liquid nitrogen and then surface-coated with a thin layer of gold prior to observation.

2.5. Characterization

The electrical conductivity was measured through-the-thickness of the unmodified epoxy polymer according to ASTM D257. For the epoxy nanocomposites containing aligned GnPs, measurements were made both parallel and transverse to the direction of alignment of the GnPs. Five measurements were taken of each material to obtain the average value and the variability. The thermal conductivity was measured using the C-Therm Thermal Conductivity Analyzer employing the modified transient plane-source (MTPS) technique. Rectangular samples were placed on the thermal sensors and completely covered the measuring area. Type 120° thermal joint compound was applied between the sample and the sensor to improve the heat flow. The temperature was controlled in a TPS Tenney Junior thermal chamber. The measurements at room temperature (25 °C) were performed both parallel and transverse to the alignment direction of the GnPs. Ten measurements of each sample material were performed to determine the average and variability of the thermal conductivity.

DCB tests were performed using an Instron tensile testing machine to determine the mode I fracture energy (GMC) of the adhesive joints. The DCB joints had the dimensions illustrated in Fig. S1b in the Supporting information. A sharp crack tip was formed by carefully wedging the crack opening from the tip of the 'Teflon' film. The crack opening load was applied to the specimens at a crosshead speed of 1 mm/min in accordance with ISO 25217. The load versus displacement curves were recorded and a travelling optical microscope was used to measure the crack length (a). The value of the fracture toughness (GMC) for the onset of crack propagation was calculated using the 'corrected beam' theory [26]. At least five specimens were tested for each composition to get the average value of GMC. As described above, the values of GMC were determined using two types of specimens: one where the direction of crack growth was transverse to the aligned GnPs and one where the direction of crack growth was parallel to the aligned GnPs. Fracture surfaces from randomly selected failed DCB specimens were sectioned and sputter coated with a thin layer of gold for SEM examination. Side-views of the crack tips were also examined by SEM after polishing with a fine-grade sand-paper.

3. Results and discussion

3.1. Electric field-induced alignment of GnPs

The alignment of the GnPs within the liquid epoxy resin when exposed to an AC electric field was investigated experimentally and theoretically. In-situ optical microscopy observations were carried out on the movement of the GnPs within the liquid epoxy resin. The applied AC electric field had an amplitude of 25 V/mm and a frequency of 10 kHz. Time-lapse images for the epoxy resin containing 0.054 vol% of GnPs are presented in Fig. 1, showing the formation of a chain-like graphene network in the direction of the applied electric field. A network of aligned nanoplatelets began to visibly develop after exposure to the electric field for about four minutes. A well-defined chain-like structure of GnPs extending between the positive and negative electrodes formed after ~10 min, which then developed into relatively thick bundles upon further exposure to the electric field for ~20 min. This 'chain-ing' process is the result of dipole–dipole attractions between the nanoplatelets. Due to the opposite charges at their ends, they gradually move closer and connect end-to-end, forming chain-like structures. These structures were also observed for epoxy resin mixtures with higher contents of GnPs (see Fig. S2). Similar chained structures have been observed for other inclusions including ceramic (BaTiO3) particles [27], carbon nanotubes [10,11], carbon nanofibers [12,13], carbon black [14], and carbon nanococones [28].

Fig. 2a and b show representative SEM and TEM images of the microstructure of the epoxy/GnPs (0.54 vol%) nanocomposite prepared without the application of the electric field. As expected, the GnPs were randomly-oriented and distributed in the epoxy polymer. Fig. 2c and d show the microstructure of the epoxy/GnPs (0.54 vol%) nanocomposite following exposure to the electric field, and most of the GnPs are aligned very close to being parallel to the applied electric field direction. Alignment of the GnPs was observed for all the different volume contents that were studied (i.e. 0.27, 0.54, 0.81 and 1.08 vol%). Voids and dispersed multi-layered GnPs are also observed in the TEM images, as indicated by the arrows in Fig. 2d. The appearance of the voids could be due to the relatively high stresses generated during the ultramicrotoming used to prepare the TEM samples [29,30]. To confirm this suggestion, selected area electron-diffraction (SAED) was employed to distinguish the GnPs from the amorphous epoxy polymer matrix, and Fig. S3 gives such an example. A well-defined diffraction spot pattern was obtained from the region close to the voids indicating the presence of crystalline GnPs.

3.2. Physical mechanisms of electric field-induced alignment of GnPs

3.2.1. Rotation

When subjected to a sinusoidal alternating electric field, a solid inclusion in a dielectric liquid is polarized and gains a dipole moment due to the different dielectric properties and electrical conductivity between the inclusion and the liquid [19]. The polarization moment, μ, is generally not aligned with the electric field for materials which are crystalline or show shape anisotropy and thus a torque T = μ × E is induced to act on the inclusion. Two-dimensional GnPs have shape anisotropy and the polarization moment parallel to the platelet is much higher than that perpendicular to the platelet. GnPs can be considered as very thin oblate spheroids with semi-major and semi-minor axes a and b, corresponding to the radius and half thickness of a graphene nanoplatelet, respectively. The overall torque acting on an inclusion is the superposition of the torques induced by fields parallel and perpendicular to its axes:

\[
T = \mu \parallel E - \mu \perp E,
\]

where \( E \parallel = E \cdot \sin \theta \) and \( E \perp = E \cdot \cos \theta \) with \( \theta \) being the angle between the electric field direction and the semi-major axis of the inclusion. The subscripts \( \parallel \) and \( \perp \) refer to the perpendicular and parallel to the surface of nanoplatelets, respectively.

When an inclusion is subjected to a sinusoidal alternating electric field \( E = E_0 \cdot \sin \omega t \), the torque acting on it is given by [31]:

\[
T = \frac{2\pi a^2 b}{3} E_0^2 \sin^2 \omega t \sin 2\theta \left[ \frac{\varepsilon_m (\varepsilon_i - \varepsilon_m)^2}{\varepsilon_m + (\varepsilon_i - \varepsilon_m)\varepsilon_i} \right]
\]

where \( L_i \) is the depolarization factor along the major axis, and \( L_i = \frac{\xi_i}{\xi_i + \frac{\gamma_i}{\gamma_i}} \) for an oblate-shaped inclusion. The subscripts \( i \) and \( m \) refer to the inclusion (i.e. the GnPs) and matrix, respectively. The term \( \xi \) is the generalized dielectric constant, \( \varepsilon_i = \varepsilon_i + j(\varepsilon_i'' + \sigma_i/\omega) \), with \( \varepsilon_i', \varepsilon_i'', \) and \( \sigma \) denoting the real part and imaginary part of relative dielectric constant and the electrical
conductivity of the inclusions, respectively. The variables \( \omega \) and \( E_0 \) denote the angular frequency and amplitude of the applied electric field, respectively.

For a GnP of relatively high electrical conductivity exposed to an AC electric field of a low to moderate frequency \( (\omega \ll \sigma) \), \( \varepsilon_i / \varepsilon_m \rightarrow \infty \), the torque can be simplified to: 

Fig. 1. Optical micrographs of GnP\( s \) in the liquid epoxy resin (0.054 vol%) during the application of the AC electric field (25 V/mm): (a) Randomly-oriented GnP\( s \) before the field was applied; (b), (c), and (d) after the field was applied for 4 min, 10 min, and 20 min, respectively. (The positive and negative electrodes are indicated by “+” and “−”.)

Fig. 2. SEM (a) and TEM (b) images of the epoxy nanocomposites with 0.54 vol% of randomly-oriented GnP\( s \); SEM (c) and TEM (d) images of the epoxy nanocomposites with 0.54 vol% of aligned GnP\( s \). The direction of the electric field (E) alignment is indicated in (c) and (d).
\[ T' = \frac{4\pi a^3}{3} \frac{\varepsilon_m}{(\beta - \beta_0)} E_0^2 \sin^2 \theta \sin 2\theta \] (3)

The electric field-induced torque is the driving force for the rotation of the GnP in the liquid epoxy resin, which is resisted by viscous drag from the epoxy resin. The time needed to rotate GnP from the initial angle \( \theta_0 \) to an angular position \( \theta \) can be estimated by balancing the electric field-induced torque with the viscous torque acting on the GnP. The viscous torque \( T' \) is proportional to the angular velocity \( \dot{\theta} \) and viscosity \( \eta \) of the epoxy resin, and can be calculated using [10,32]:

\[ T' = -\eta \dot{\theta}, \] (4)

where \( k_r \) is the rotational friction coefficient and \( k_r = 32a^3/3 \) [32]. Now the dynamic condition \( T' = T'' \) yields,

\[ \dot{\theta} = -\frac{\pi}{8\eta} \frac{\varepsilon_m}{(\beta - \beta_0)} E_0^2 \sin^2 \theta \sin 2\theta \] (5)

from which the time to rotate (\( t_r \)) a GnP from the initial angle \( \theta_0 \) to a generic angular position \( \theta \) can be solved from the following transcendental equation:

\[ t_r = \frac{1}{2\omega_0} \sin 2\omega t = \frac{1}{A} \ln \frac{\tan \theta_0}{\tan \theta} \] (6)

where:

\[ A = \frac{\pi}{8\eta} \frac{\varepsilon_m}{(\beta - \beta_0)} E_0^2 \] (7)

By setting the final angle \( \theta \) close to zero, the corresponding value is the rotation time for a GnP with an initial angle \( \theta_0 \). Eq. (6) reveals that the rotation time is dependent on the frequency of the AC electric field, but this effect diminishes rapidly as the frequency increases, with the rotation time approaching the following lower bound,

\[ t_{r,\infty} = \frac{1}{A} \ln \frac{\tan \theta_0}{\tan \theta} \quad \omega \to \infty \] (8)

It should be noted that numerical solutions for Eq. (6), referring to Fig. S4d, reveal that when the angular frequency of the AC electric field exceeds \( 1/t_{r,\infty} \), the rotation time approaches within 95% of that given by Eq. (8), as will be discussed in Section 3.2.3.

3.2.2. End-to-end connection (i.e. 'chain' formation)

Once rotated, polarized GnP tend to attract each other due to the opposite charges present at their ends. By balancing the electric force and the translational viscous friction, it is possible to estimate the time required to form an end-to-end connection between two plates. The electric charge (\( q \)) present at the opposite ends was evaluated by considering the torque as the product of charges at the ends of nanoplatelets and the distance of \( 2a \) (i.e. the diameter) such that:

\[ T' = q \times E \times 2a \sin \theta \] (9)

This torque induced by the applied field is given in Eq. (2), based on which the total electric charge at the end of a disk-shaped nanoplatelet is estimated by:

\[ q = \frac{T'}{E_2 a \sin \theta} = \frac{2\pi a b}{3} E_0 \sin \theta \cos \theta \frac{\varepsilon_m (\varepsilon_1 - \varepsilon_m)}{\varepsilon_m + (\varepsilon_1 - \varepsilon_m) k_s} \] (10)

Thus, the electric force attracting adjacent nanoplatelets is:

\[ F_{el} = \frac{q^2}{4\pi E_0 x^2} = \frac{\pi (ab)^2}{9\varepsilon_0 x^2} E_0^2 \sin^2 \theta \cos^2 \theta \left( \frac{\varepsilon_m (\varepsilon_1 - \varepsilon_m)}{\varepsilon_m + (\varepsilon_1 - \varepsilon_m) k_s} \right) \] (11)

When a nanoplatelet becomes parallel to the electric field, i.e. \( \theta = 0 \), the electric force attracting two nanoplatelets separated by \( x \) is given by:

\[ F_{el} = \frac{\pi (ab)^2}{9\varepsilon_0 x^2} E_0^2 \sin^2 \theta \cos^2 \theta \left( \frac{\varepsilon_m (\varepsilon_1 - \varepsilon_m)}{\varepsilon_m + (\varepsilon_1 - \varepsilon_m) k_s} \right)^2 \] (12)

Coupling this electric force with the translational viscous friction, the equation representing the translational motion is:

\[ \frac{\pi (ab)^2}{9\varepsilon_0 x^2} E_0^2 \sin^2 \theta \cos^2 \theta \left( \frac{\varepsilon_m (\varepsilon_1 - \varepsilon_m)}{\varepsilon_m + (\varepsilon_1 - \varepsilon_m) k_s} \right)^2 = -\eta k_x x \] (13)

where \( k_x \) is the translational friction coefficient for an oblate spheroid particle [33,34], and is:

\[ k_x = 6\pi(a^2b)^{1/3} \left( \frac{\sqrt{b/a} - 1}{\sqrt{b/a} + 1} \right) \] (14)

The governing equation for the translation motion can be rewritten as:

\[ \ddot{x} = -\frac{B \sin^2 \theta}{x^3} \] (15)

where:

\[ B = \frac{4\pi a^3}{9\eta k_\omega (\beta - \beta_0)} E_0^2 \] (16)

Solving the differential Eq. (15) yields the following solution:

\[ x(t) = \sqrt{\frac{3}{2} B t + x_0^2} + x_0 \] (17)

Similar to the solution of the rotation time described in Section 3.2.1, the lower-bound solution pertinent to the high frequency limit is:

\[ x(t) = \sqrt{\frac{3}{2} B t + x_0^2} \] (18)

where \( x_0 \) is the initial distance from two opposite charged ends of graphene. The time required for the formation of an end-to-end connection (\( t_c \)) is:

\[ t_c(x_0) = \frac{2x_0^3}{3B} \] (19)

The influence of frequency diminishes when the frequency exceeds \( 1/t_c \). The initial distance \( x_0 \) between the closest opposite charged ends of graphene can be evaluated by using similar method as that applied by Monti et al. for carbon nanotubes [10]. This distance depends on the content of the GnP in the epoxy resin. Assuming the graphene is uniformly dispersed in the whole volume of the epoxy, the portion of this volume for each GnP (\( V_c \)) can be evaluated by:

\[ V_c = \frac{1}{\rho} \frac{W_c}{m_c} \] (20)

where \( \rho \) is the density of the epoxy, \( W_c \) is the weight fraction of graphene, and \( m_c \) is the mass of each GnP. The volume containing one GnP can be modeled as a square cuboid, with its two edges being equal to the average diameter \( (2a) \) of GnP, and its third edge being the average initial distance \( x_0 \). In this case, the average initial distance can be obtained from the volume given by Eq. (20):

\[ x_0 = \frac{V_c}{4a^2} = \frac{1}{\rho} \frac{W_c}{m_c} \frac{1}{4a^2} \] (21)
3.2.3. Model results

Using the above analysis, it is possible to calculate the time required to rotate the GnP and to form an end-to-end connection in the liquid epoxy resin in the direction of the electric field. In the calculation of the rotation time, the final angle was set at a value slightly greater than 0° (i.e. 1.0°), otherwise the calculated alignment time approaches an infinite value. The GnP have an approximate thickness (b) of 8 nm and diameter (a) of 25 μm. The values of the viscosity and relative dielectric constant of the liquid epoxy resin were taken for the calculations to be ƞ = 0.725 Pa·s and \( \varepsilon = 3.6 \times 10^9 \) with \( \varepsilon_0 \) being the vacuum permittivity. Fig. 3d shows the calculated time required for the electric field to align the nanoplatelet from various initial angles (\( \theta_0 \)) to the final angle of \( \theta = 1.0° \). The calculated curve shows a similar trend to that recently reported by Monti et al. [10] for direct current field-induced alignment of carbon nanotubes. Fig. 3d shows that with the applied electric field strength of 25 V/mm, amplitude of 10 kHz, it takes up to ~15 min to closely align the majority of nanoplatelets upon applying the electric field.

In the calculation of the time required to form an end-to-end connection between two GnP, the mass of a single GnP (2.65 × 10^{-14} kg) was estimated by calculating how many carbon atoms were present in the single sheet having the dimension of 25 μm × 25 μm and then multiplying this by the number of layers of sheets per nanoplatelet [10]. The GnP are on average 8 nm thick which equates to about 18 single sheets of graphene based on the d-spacing (taken as 0.34 nm). For a liquid epoxy resin containing 0.1 wt% (0.054 vol%) of GnP, the average initial separation distance \( x_0 \) between two platelets is ~36 μm. Fig. 3e shows the plot of Eq. (18). It can be seen that the time needed for a GnP to move a distance of 36 μm was about four minutes which is consistent with the optical microscopy observations shown in Fig. 1.

A thorough analysis of Eqs. (6) and (18) reveals the effects of different variables on the alignment of GnP in a polymer. Firstly, as expected, it takes a shorter time to rotate GnP and to translate a distance (\( x_0 \)) to form end-to-end connection if the viscosity of the epoxy/GnP mixture is lower and/or a stronger electric field is applied (see the plots in Figs. S4 and S5). The role of the aspect ratio (a/b) of the filler is presented in Figs. S4c and S5c. The contribution of this parameter seems to be negligible, i.e. the orientation time and end-to-end connection time does not change significantly as the aspect ratio of the GnP is varied. Therefore, for GnP of a given size (a), the thickness (i.e. the exfoliation state) does not significantly affect the alignment process. The influence of frequency of the electric field on the rotation time is presented in Fig. S4d. According to the model, the frequency will not have any noticeable effects provided that the frequency is moderately high (greater than 10 Hz in the present case), which is consistent with the experimental observations shown in Fig. 4. The DC conductivity was measured to monitor the degree of alignment during the alignment process every 60 s after the application of the electric field. As shown in Fig. 4, the electrical conductivity increases due to the formation of the GnP networks and reaches a plateau after around 600 s, irrespective of the frequency of the external electric field. Similar findings have been reported for epoxy/carbon black composites, i.e. the time-dependent evolution of the conductivities and final conductivity are nearly independent of frequency up to 10 kHz [14].

These experimental studies and theoretical modeling on the formation of aligned graphene platelets in both the liquid epoxy resin and the epoxy nanocomposites have indeed confirmed that a high degree of alignment of the GnP may be achieved by using the process conditions described above. The electrical and thermal conductivities, and fracture toughness of the epoxy

![Fig. 3. Alignment mechanisms of the GnP by the AC electric field: (a) rotation and end-to-end connection of polarized GnP; (b) the initial random orientation in the epoxy resin; (c) GnP oriented along the electric field direction in the epoxy resin; (d) plot of the rotation time as a function of the initial angle for the GnP; (e) distance from two oppositely charged GnP ends as a function of time. Note: the yellow region represents the epoxy resin and the blue regions are the GnP.](image-url)
nanocomposites containing aligned GnPs have been determined and are presented in the following sections.

3.3. Electrical conductivity

The electrical conductivity of the GnPs parallel to the surface is $10^7$ S/m, which is much higher than that perpendicular to the surface (i.e. $10^2$ S/m) [35]. Thus, the AC electric field-induced alignment was expected to increase significantly the conductivities of the epoxy/GnPs nanocomposites in the alignment direction. Electrical conductivities were measured in both the liquid epoxy resin/GnPs mixture during alignment and the cured epoxy nanocomposites.

Fig. 4 shows the change in the electrical conductivities of a liquid epoxy resin containing 0.054 vol% of GnPs when subjected to the electric field of different frequencies. The electrical conductivity increased rapidly over the initial ~10 min and then reached a constant value, by which time the in-situ observation of the liquid epoxy resin/GnPs mixture showed the formation of a well-defined chain-like graphene network aligned with the direction of the applied electric field (see Fig. 1d). The initial rapid rise in the electrical conductivity is attributed to the progressive rotation of the highly conductive nanoplatelets towards the direction of the applied electric field and the subsequent chaining to form continuous, electrically conductive pathways between the electrodes.

After about 10 min the majority of the GnPs were closely aligned with the electric field direction, as predicted by the theoretical models presented in Sections 3.2.1 and 3.2.2, and therefore the electrical conductivities of the liquid epoxy resin/GnPs mixture reached a constant value.

Linear versus logarithmic plots presented in Fig. 5 show the effects of alignment and volume content of the GnPs on the electrical conductivities of the epoxy nanocomposites. The electrical conductivities of the epoxy nanocomposites containing aligned GnPs were measured in two directions. For comparison, the electrical conductivity for the epoxy nanocomposites containing randomly-oriented GnPs are also included in Fig. 5. The results demonstrate that the electrical conductivities of the aligned and randomly-oriented nanocomposites increase rapidly with the content of GnPs. Moreover, the conductivities of the epoxy nanocomposites in the alignment direction of the GnPs are significantly higher than that of the nanocomposites containing randomly-oriented GnPs. Furthermore, the conductivities of the nanocomposites along the alignment direction are consistently 2–3 orders of magnitude higher than that along the transverse direction. Anisotropic electrical properties have also been recently reported by Kim and co-workers [36,37] for epoxy/graphene aerogel composites and epoxy/graphene oxide composites where a relatively high degree of alignment was observed when the graphene content was above a threshold.

By fitting the experimental data to a power-law equation (see Fig. 5b and c), a percolation threshold ($\psi_c$) content of ~0.52 vol% was determined for the epoxy nanocomposite containing randomly-oriented GnPs. Electric field-induced alignment of the GnPs resulted in a much lower percolation threshold of ~0.22 vol% when the conductivity was measured in the alignment direction of the GnPs. This value is less than half that of the nanocomposites containing randomly-oriented GnPs. Thus, these results clearly demonstrate that aligning the GnPs significantly lowers the content of GnPs necessary to achieve percolation.

3.4. Thermal conductivity

Fig. 6 shows the effects of the volume content and alignment of the GnPs on the thermal conductivities of the epoxy nanocomposites. The thermal conductivities of the aligned epoxy nanocomposites were measured in two directions, i.e. parallel and transverse to the alignment direction of the GnPs, as indicated. The thermal conductivities of the epoxy nanocomposites containing randomly-oriented GnPs increased steadily with the content of
The content of GnPs was further increased from 0.8 vol% to 1.08 vol%. The reason for this diminishing difference at relatively high loading levels is most likely due to the reduced degree of alignment and the likely agglomeration of the GnPs at concentrations above about 0.8 vol%.

3.5. Fracture toughness

The mode I fracture toughness of the unmodified epoxy polymer and the epoxy/GnPs nanocomposites were measured using the double cantilever beam (DCB) test. The materials were tested in the form of a thin, continuous epoxy polymer layer (2 mm thick) which was bonded between two carbon fibre-epoxy composite substrates (as illustrated in Fig. S1b in the Supporting information). In all the tests, the crack propagated through the epoxy polymer layer and did not grow along the epoxy polymer-substrate interface or within the carbon fibre-epoxy composite substrates.

The effects of alignment and volume concentration of the GnPs on the fracture toughness ($G_{IC}$) of the epoxy nanocomposites are shown in Fig. 7. The fracture toughness of the nanocomposite containing randomly-oriented GnPs increased at a quasi-linear rate up to ~0.8 vol%, above which the rate of improvement tapered off. When the GnPs were aligned in the transverse direction with respect to the crack growth direction, the values of toughness increased linearly with the content of GnPs up to about 0.8 vol%. (It should be recalled that the electric field was applied transversely to the subsequent crack growth direction to make the GnPs align perpendicular to the crack growth.) Such alignment of the GnPs induces a significantly stronger toughening effect of about 40% compared to the randomly-oriented epoxy nanocomposites. By contrast, a lower toughness (of about 10–15% compared to the randomly-oriented materials) was measured when the GnPs were aligned parallel to the crack growth direction. Further, there was no statistically significant difference observed in the toughness of the epoxy nanocomposites containing randomly-oriented and aligned GnPs when the volume concentration of GnPs was increased from 0.8 vol% to 1.08 vol%. This may be ascribed to the reduced degree of alignment and the increased agglomeration of the GnPs at contents above about 0.8 vol%. Since, at relatively high contents of nanofillers, the viscosity of the epoxy mixture and the degree of filler packing increase. These factors make it more difficult for the GnPs to move and rotate in response to the applied electric field. Similar behaviour has been reported for multi-walled carbon nanotubes in an epoxy polymer matrix [40].

The improvement in fracture toughness gained by aligning the GnPs transverse to the crack growth direction, is superior to the toughening efficiency reported in the literature for various types of graphene when added to epoxy polymers. Table S1 summarizes the published values for the percentage increase in the mode I fracture toughness of epoxy polymers containing different randomly-oriented graphene-based materials (i.e. graphene oxide (GO), thermally expanded or reduced GO, chemically-modified graphene, or graphene foam) [4,6,29,30,41–47]. The maximum percentage increase in the fracture toughness (i.e. of up to ~900%) from the present studies is the highest recorded improvement. This demonstrates the very high toughening efficiency gained by the AC electric field-induced alignment of the GnPs, while at the same time providing the additional functionalities of increased electrical and thermal conductivities.

3.6. Toughening mechanisms

Fractographic analysis of the DCB specimens was performed to determine the toughening mechanisms induced by both the randomly-oriented and aligned GnPs. Fig. 8 shows a side-view of the main crack front in the unmodified epoxy polymer and in an epoxy nanocomposite containing randomly-oriented and

![Fig. 6. Effects of the volume content and alignment of the GnPs on the thermal conductivities of the epoxy nanocomposites. (The direction of the measured thermal conductivity with respect to the alignment direction of the GnPs is indicated.)](image1)

![Fig. 7. Effects of the volume content and alignment of GnPs on the mode I fracture energy ($G_{IC}$) of the epoxy nanocomposites. (The alignment direction of the GnPs with respect to the crack growth direction is indicated.)](image2)
aligned GnP s. The crack tip in the unmodified epoxy polymer (see Fig. 8a) is well-defined, and there is no evidence of discrete damage processes ahead of the crack, and this observation is typical for brittle-like polymers with relatively low values of fracture toughness. In contrast, the fracture process at, and immediately ahead of the main crack tip was altered by the addition of the GnP s (see Fig. 8b and c). In addition, the crack path has changed from being relatively flat and straight to being very tortuous, which is particularly noticeable for the composites containing aligned GnP s (Fig. 8c). There were no visible differences in the crack path for the nanocomposites containing GnP s aligned parallel or transverse to the crack growth direction.

The fracture and toughening processes induced by the presence of the GnP s are shown schematically in Fig. 9, and the evidence for this schematic is given in Figs. 8, 10 and 11. Discrete microcracks (typically of the size of the GnP s, i.e. ~10–25 µm long) were created immediately ahead of the main crack within the nanocomposites (see Fig. 10b). The microcracks initiated at the epoxy/GnP s interfaces due to the stress concentrations created by the mismatch in the Young’s modulus and Poisson’s ratio of the graphene and the epoxy polymer. In addition, as evidenced in Fig. 11, microcracks also developed due to delamination between the nanosheets within the GnP s and interfacial debonding of the GnP s from the epoxy polymer matrix. This indicates the relatively weak bonding between the graphene sheets and at the epoxy-graphene interface that occurs when GnP s are used without any functionalization. The formation of microcracks ahead of the main crack is an intrinsic toughening mechanism which increases
the fracture resistance of low toughness materials [48], and this would account, in part, for the higher toughness of the epoxy nanocomposites.

Fig. 10c shows that the discrete microcracks coalesced into a multi-branched network of longer cracks which then connected with the main crack front. This is also an effective intrinsic toughening process which contributes to the increase in the fracture toughness of the nanocomposites. Fig. 56 shows the crack surfaces of the epoxy nanocomposites with increasing content of GnPs, and there is a progressive increase in surface roughness attributed to the increased degree of crack bifurcation and branching. Again these toughening mechanisms will increase the toughness of the epoxy nanocomposites. Furthermore, the orientation of the GnPs at some inclined angle to the crack growth direction will obviously increase the probability of the main crack encountering them and thus induce more crack deflection and branching. Hence, the presence of a relatively high level of inclined GnPs, approximately transverse to the crack growth direction, will provide an enhanced toughening effect in the epoxy nanocomposites. Indeed, examination of the crack tip at high magnification (Fig. 10d) revealed fracture and pull-out of GnPs, and crack bridging by the pulled-out GnPs. The transversely-aligned GnPs tended to initially bridge the crack over a crack-opening distance of up to ~20 μm, which is equivalent to the size of the nanoplatelets. As the crack propagated along the DCB specimen, the GnPs fractured and pulled-out from the epoxy polymer matrix. These very effective extrinsic toughening mechanisms, which are not significant in the epoxy nanocomposites containing randomly-oriented GnPs or GnPs aligned parallel to the crack growth direction, account for the more effective toughening.

4. Conclusions

The application of an AC electric field has been shown to align GnPs, and to drive the GnPs to form a chain-like network.
nanostructure, in an epoxy polymer along the electric field direction. Theoretical modeling has indicated that the time required for the GnPs to rotate and form end-to-end ‘chain’ connections, when the epoxy resin is in its liquid phase, may depend on the aspect ratio of the GnPs, the viscosity of the mixture, and the strength and frequency of the applied electric field. The lower the viscosity and the stronger the applied electric field, then shorter is the time it takes to align the GnPs. The aspect ratio \((a/b)\) of the GnPs and the frequency of the applied electric field have negligible effects on the rotation and chain-formation time.

Compared to the unmodified epoxy polymer, a significantly higher electrical conductivity (of up to about 7–8 orders of magnitude) and thermal conductivity (of up to nearly 60%) have been achieved in the alignment direction of the GnPs. Moreover, aligning the GnPs transverse to the crack growth direction has dramatically improved the fracture toughness (of up to nearly 900%). These properties are far superior to those achieved by randomly-oriented GnPs. Both intrinsic and extrinsic toughening mechanisms have been identified as the major factors responsible for the remarkable increase in fracture toughness. Specifically, the main intrinsic toughening mechanisms for the epoxy nanocomposites containing transversely-aligned GnPs include micro-cracking and debonding of the GnPs, pinning and deflection of the main crack. The extrinsic toughening mechanisms include pull-out of and bridging by the GnPs. The orientation of the aligned GnPs transverse to the crack direction increases the probability of interactions occurring between the advancing crack tip and the GnPs. This greatly enhances the effectiveness of the extrinsic toughening mechanisms and leads to a significant increase in the fracture toughness compared to those containing GnPs aligned parallel to the crack growth direction or randomly-oriented GnPs. The differences in the properties between the epoxy nanocomposites containing randomly-oriented GnPs and aligned GnPs become less marked when the content of the GnPs increases to above about 0.8 vol%. This may be ascribed to the increased agglomeration and reduced degree of alignment of the GnPs at contents above about 0.8 vol%.

The present work has clearly demonstrated that an AC electric field can be applied to control the orientation and alignment of GnPs in an epoxy resin and therefore enables the fabrication of high-performance, multifunctional epoxy/graphene nanocomposites.

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Appendix A. Supplementary data

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References