Abstract

The tensile and flexural behaviour of a graphene nanoplatelet (GnP) reinforced polymer, Grade M25 GnP/Araldite LY564 is experimentally investigated. This is followed by a multi-scale finite element model to simulate the tensile response as the most critical loading case. The approach is based on the multi-scale method and consists of a unit cell and a representative volume element (RVE). At the unit cell level, the material nanocharacteristics (filler geometry, phase mechanical properties, interfacial properties) are used to calculate the local tensile response. The material architecture is simulated at the RVE level by distributing the locally obtained unit cell mechanical properties, using periodic boundary conditions. A statistical sample was studied and the average mechanical characteristics were compared to the macroscopic measured stress–strain data. Finally, the simulation methodology was validated by comparisons between the effective experimental and numerical results.

1. Introduction

The high stiffness and strength properties of graphene platelets have drawn extensive attention from researchers worldwide. A massive number of studies have been carried out to study the reinforcing effect of graphene in polymer matrices [1–10]. It has been reported though that the final mechanical properties of nanocomposites can be affected by various factors, such as the inherent properties of matrices and fillers, the shape, size, aspect ratio and volume fraction of fillers, the interaction between fillers and matrices creating an interphase, the composite’s fabrication method, which can affect uniform dispersion, introduce voids and other imperfections and hence reduced performance.

The effect of graphene dispersion was investigated by Tang et al [2], while Wang et al [3] explored the effect of graphene nanoplatelet (GnP) size on tensile and flexural modulus and strength of a GnP/epoxy nanocomposite. The influence of the manufacturing parameters on the performance of a GnP/epoxy nanocomposite was studied in detail by Pullicino et al [5] and Poutrel et al [6]. The former examined the effect of shear mixing speed and time on mechanical properties, while the latter reported the effect of the functionalization of nanoparticles, as well as the alignment of GnP into the epoxy by an electrical field on mechanical, electrical and thermal conductivity. Later, King et al [4] fabricated neat aerospace epoxy along with two different types of GnP to evaluate their tensile properties using typical macroscopic measurements and determine modulus and creep compliance through nanoindentation. GnP/silicone rubber composites were prepared by Song et al [1], to record a significant increase of the tensile strength with the addition of a low content of GnP. In addition to this, Minh-Tai Le et al [9] successfully fabricated a hybrid polymer nanocomposite containing epoxy/polyester blend resin and GnP, indicating increased tensile strength of the nanocomposite material with the addition of 0.2 wt% GnP. Graphene nanosheet/aluminium nitride (AlN) composites were prepared by hot-pressing and the effect of graphene nanosheets on their microstructural, mechanical, thermal and electrical properties were investigated in the work of Yun et al [10].
Summarising the available literature on the experimental exploration of graphene nanocomposites, the manufacturing process is time and cost consuming, while the final properties are sensitive to several factors (particle size and purity, functionalisation and chemistry, particle-matrix bonding, dispersion as a result of fabrication parameters). Therefore, some computational studies have been carried out to examine the mechanical behaviour of nanocomposites and develop design guidelines in an effort to optimise selected constituents and improve nanocomposite performance with reduced experimental effort.

Bansal et al [11] showed that the thermomechanical properties of ‘polymer nanocomposites’ were quantitatively equivalent to the well-documented case of planar polymer films, while a novel hybrid numerical-analytical modelling method was presented by Liu et al [12], which predicted viscoelastic behaviour of multiphase polymer nanocomposites, by combining the finite element technique and a micromechanical approach. The mechanical reinforcing efficiencies of two types of nanoparticles, nanotube and nanoplatelet, were compared from a micromechanics perspective by Liu et al. The nanocomposites were modelled as two-phase materials (nanoparticles and matrix) to evaluate the stiffness increment of the composite, accounting for their volume fraction, aspect ratio and orientation. Cho et al [13] used the Mori–Tanaka approach in conjunction with molecular dynamics to predict the mechanical properties of epoxy reinforced with randomly oriented graphite platelets. In detail, the calculation of elastic constant of graphite nanoplatelets was based on their molecular force field, and was incorporated into a Mori–Tanaka micromechanical analysis. The predicted moduli were compared with experimental results of several nanocomposites with graphite particles. Experimental as well as theoretically-based hierarchical multi-scale procedures for the evaluation of the effective elastic modulus of polylactide (PLA)/expanded graphite (EG) nanocomposites were developed by Mortazavi et al [14]. In the multi-scale modelling, molecular dynamics were utilised for the evaluation of the elastic stiffness tensors of expanded graphite, with two-phase continuum modelling tools developed by means of finite elements for the evaluation of the elastic modulus of a representative volume element (RVE) of PLA/EG nanocomposite. Pandele et al [15] performed molecular mechanics and dynamic simulations at atomistic scale to investigate the mechanical behaviour of the graphene-based chitosan (CS) composite with varied reinforcing content. Although Yi Hua et al [16] did not consider graphene/polymer nanocomposites, their work on the simulation of the mechanical response of silica/epoxy nanocomposite gave insight into the effect of the interphase developed between the epoxy and a nanoparticle. Finally, Spanos et al [17] described a micromechanical finite element approach for the estimation of the elastic mechanical properties of graphene-reinforced composites. Modelling of the reinforcement was based on its atomistic microstructure by describing graphene as a space frame in which the carbon (C) atoms are represented by nodes, while the matrix was approached as a continuum. Spring-based finite elements were used for the simulation of the discrete geometric structure and behaviour of each graphene layer. In particular, spring elements were considered to simulate the C-C bond stretching, angle bending and twisting by transforming the interatomic potential energy to spring element, as described in detail in the work of [18]. The load transfer conditions between the graphene and the matrix were modelled using joint elements connecting the two materials, simulating the interfacial region. The study on the effect of interface on mechanical behaviour and stress-transfer was extended in later work by Spanos et al [19]. Although this work simplifies the approach of the mechanical behaviour of graphene nanocomposite, it is limited by the size of the structure, the complexity of the model and the simulation of the effect of the micro-/macroscopic parameters on the material mechanical performance (dispersion method, multi-layer particles of different sizes, etc) and its statistical characteristics. With a similar trend, Guo et al [20] suggested a multi-scale method, where the graphene is a space frame structure and the C-C bonds are represented with nanoscale beams. Papadoyopoulos et al [21] presented a stochastic finite-element-based methodology in multiple scales for modelling the mechanical performance of graphene-reinforced nanocomposite. They proposed an equivalent shell element that can be used as an effective surrogate to the corresponding detailed molecular mechanics models of graphene. The graphene-shell element was embedded into a 3D solid element-represented polymer matrix, while cohesive zone elements were employed for the simulation of delamination and debonding phenomena on the graphene/polymer interface. A stochastic analysis was conducted on the effect of the random wrinkling of single-layered graphene on the overall behaviour of the nanocomposite. The evolution of these simulation approaches was presented by Parashar and Mertiny [22], who combined the atomistic modelling of graphene, the continuum polymer matrix and the virtual crack closure technique to predict the effect of graphene on the strain energy release rate for a crack lying in a polymer.

The aforementioned numerical methods could be summarised by a general scheme consisting of an atomistic model simulating local phenomena and solved with molecular dynamics processes, and a macroscopic model approaching the material architecture was usually solved with finite element analysis. Although atomistic/molecular dynamics is able to simulate accurately the local phenomena, it is time consuming and includes complicated calculations demanding inputs related to atoms, atom-atom and atom-molecule interaction. Therefore, these are not considered appropriate for quick engineering design decisions.
The aim of this research project is to develop numerical simulations to describe the mechanical response of a GnP/polymer nanocomposite, by using a commercial finite element package. Industrial engineers could apply the proposed approach to design nanocomposites, serve specific needs and simulate the response of big structures whose experimental testing is constrained by time and cost. An engineering tool is developed to characterise the mechanical response of graphene nanoparticles/polymer nanocomposites utilising the effective macroscopic information of the material while being able to account for multiple parameters affecting its performance (filler geometry/size, functionalisation, dispersion, etc) on a flexible, customisable scheme avoiding expensive and time-consuming trial and error experiments.

In this paper, a multi-scale finite element model is developed to estimate the mechanical properties of GnP/polymer nanocomposites and compare them to experimental results under generic comparisons. In generic comparisons, the comparison/validation is limited to checking the response values (temperature, displacement, strain, etc) at a number of critical locations, known as ‘hotspots’, and/or checking macroscopic/effective material properties/response. The simulation is performed within a unit cell and an RVE. At the unit cell level, the material nanocharacteristics (filler geometry, phase mechanical properties, interfacial properties) are used to calculate the local mechanical response. The material architecture is modelled at the RVE level by distributing the unit-cell-obtained local mechanical properties. The numerical analysis results are compared to the experimental performance of GnP/epoxy nanocomposites fabricated during this research work.

2. Experimental procedure and test results

2.1. Materials
For the sample preparation, Grade M25 GnP GnPs acquired by XG Sciences [23] were used in a powder form. The nanoparticles exhibited an average thickness of 6–8 nm, an average length of 25 μm and a typical surface area of 120–150 m² g⁻¹. The graphene characteristics were obtained by independent experimental studies, as presented in [5, 24]. The nanoparticles were combined with a polymeric matrix based on a low-viscosity bisphenol-A epoxy resin (Araldite LY564) and a cycloaliphatic polyamine curing agent (Aradur 2954) with a mixing ratio of 100:35 (epoxy: hardener) supplied by Huntsman [25]. The nanocomposite specimens obtained had a volume fraction ranging between 1% and 7.5%, while neat epoxy specimens were manufactured as a baseline used for comparisons.

2.2. Manufacturing process
At first, the GnP were added to acetone, forming a solution with a concentration of 50 mg ml⁻¹. The solution was placed in a sonication bath for 30 min to dissolve the particles stacks of the powder. Afterwards, liquid epoxy was added to the solution, which was shear mixed at 3000 rpm for 1 h, while being heated at 80 °C to reduce the viscosity. By the end of the process, the presence of residual acetone was checked and any remains were evaporated by hot-stirring of the mixture at 80 °C. Then, the solution was allowed to reach room temperature and the hardener was added. The final mixture was stirred for 5 min at 1000 rpm followed by degasification and transfer to a silicone rubber mould with the aid of a syringe. The material system was cured at 80 °C for 2 h and post-cured at 140 °C for 8 h. All the specimens were surface ground to obtain flat surfaces and uniform thickness.

2.3. Scanning electron microscopy (SEM)
In this research, SEM was employed to observe and analyse the dispersion and the interface (and any interphase) between the GnP filler and matrix. The fracture surfaces of the samples tested under tensile loading were also observed under SEM at 5 kV accelerating voltage. The samples were cut and fixed on stubs with copper tape and then coated with silver using a Quorum Q150T ES machine.

In these images, the filler geometry, polymer fracture surface and interfacial interaction between reinforcement and matrix can be visualised. The fracture surface of 1.0 wt% nanocomposite is presented in figure 1. Due to the low filler loading, it is easy to observe the polymer fracture surface. The fracture of polymer is characterised by plastic yielding and the material slip planes (maximum shear stress plane) could be seen. Examples of these formations could be spotted in the green circles of figures 1(c) and (d) while similar ones could be found in figures 2(b) and (d). As far as the reinforcement shape and geometry are concerned, the result of the manufacturing process on the nanocomposite structure could be noted in the SEM images. At first, the GnP are not flat but exhibit a 3D waviness (cyan dotted lines in figures 1(b)–(d) and 2(d)). The particles exhibit a range of shapes from rectangular (figure 2(b)) to circular ones (figure 2(c)). Last but not least, important information could be derived from the SEM images about the interfacial interaction between the polymer and the filler. Around the GnP particles, the polymer is damaged with obvious signs of cracking and debonding. The debonded areas are highlighted in the images with yellow/black hatched patterns (figures 1(b)–(d) and 2(d)).
These observations indicate weak interfacial interaction and it is expected to be the main damage that leads to ultimate fracture of the tested specimens [6].

2.4. Mechanical characterisation—tensile testing

Tensile tests were performed on an Instron 3344 universal testing machine at room temperature following the ASTM D638 standard test method. A 2000N load cell was used in this experiment, and the speed of the crosshead was 3 mm min\(^{-1}\). The strain was obtained by an MTS contact extensometer, which was set on the specimens during the test. The type of the specimen tested in this project was type IV specimen according to ASTM D638 standard; five specimens were tested and the results were averaged, reporting coefficient of variation.

Typical tensile stress–strain plots for pure epoxy and GnP/epoxy nanocomposite samples are presented in figure 3. The elastic modulus is improved with increasing GnP content, while the tensile strength and fracture strain both decrease with GnP volume fraction. The average values of these mechanical properties and their standard deviation are summarised in figure 4. The elastic modulus increases with GnP loading lower than 5%, while it decreases when GnP loading is 7.5%. By increasing the filler content, the viscosity of the nanofluid is increased, the dispersion quality is not improved and the probability of agglomeration formation and size also increases. As a consequence, the improvement of elastic response by the GnP reinforcement is reduced by the inadequate dispersion and agglomerations present. In terms of tensile strength, it is governed by the phase strength, filler dispersion and interphase that developed between the matrix and the polymer. In SEM images of the fracture surface presented in figures 1(b)–(d) and 2(d), the GnP particles are not fractured, while damage and cracks are noted on the interface between the GnP and epoxy. This indicates a weak interfacial interaction dominating the fracture phenomena. The filler, therefore, does not enhance the material strength, but acts as an inclusion inducing stress concentration on its perimeter. By increasing the filler content, the stress and damage concentration points in the material structure increase as well, reducing the tensile strength.

A comparison between the obtained experimental data with a data set available in the literature [6] was made and presented in figure 5. Both tensile modulus and strength exhibit a similar trend to the literature experimental data. The most important discrepancy is noted for the tensile modulus of 5 wt% GnP loading. Any other difference between the two data sets could be attributed to the statistical nature of the nanocomposite.

Figure 1. SEM images on the fracture surface of 1.0 vol% GnP/epoxy nanocomposite under tensile loading. (b)–(d) are details of the original image (a). Green circles denote the areas of plastic yielding and material slip planes. Yellow lines indicate filler–matrix debonded areas, while light cyan dashed lines outline the GnP profile.
mechanical properties and their viscoelastic/viscoplastic performance as a consequence of the different crosshead speed.

2.5. Mechanical characterisation—three-point bending testing

Bending tests were performed on an Instron 3344 universal testing machine at room temperature based on the ASTMD7264 standard test method (three-point bending). Specimens were bent by a 100 N load cell with a moving speed of 1 mm min$^{-1}$ and the loaded span was 80 mm. The rectangular specimens had the dimensions of 154 × 13 × 4 mm; five specimens were tested and the data averaged.
At first, the stress–strain curve for every weight fraction is presented in figure 6. Similar to the tensile response, GnP improves the elastic flexural modulus of the nanocomposite, while its bending strength is decreased. The maximum tensile strain of the outer surface occurs at mid-span and can be calculated by

\[ \epsilon_{\text{max}} = \frac{M}{EI} \]

where \( M \) is the maximum bending moment, \( E \) is Young's modulus, \( I \) is the second moment of area, and \( \epsilon_{\text{max}} \) is the maximum strain.
equation (2), where $\delta$ is the mid-span deflection, $L$ is the support span and $h$ is the beam thickness. Similarly, the maximum stress at the outer surface at mid-span is determined by with $P$ being the applied force at the mid-span. Finally, the bending modulus (or flexural secant modulus of elasticity) is given with $m$ being the slope of the secant of the force-deflection curve ($P-\delta$). The bending modulus and strength for each case is summarised in figure 7. Regarding bending modulus, a fluctuation could be noted with minimum bending modulus found for 2.5 wt% filler content. The bending strength decreases monotonically with filler concentration. This behaviour could be attributed to the same mechanisms as the ones already stated for the tensile properties, inadequate filler dispersion and extensive agglomeration that damage performance. It is important to mention that the bending modulus and strength are higher than those obtained by uniaxial tensile loading, where the whole volume of the material experiences uniform stress; in bending, half of the material is loaded in compression (linear variation of direct stress through specimen thickness).

\[
E_{\text{sec}}^L = \frac{L^3m}{4bh^2},
\]

\[
\varepsilon = \frac{6\delta h}{L^2},
\]

\[
\sigma = \frac{3PL}{2bh^2}
\]

3. Numerical model and results

A multi-scale finite element model is developed to predict the tensile properties of GnP/epoxy nanocomposites based on observations of the experimental material characterisation of section 2. It consists of a unit cell estimating the local material response and an RVE simulating the material response according to its architecture.

3.1. Unit cell

A unit cell is built to simulate the effect of the reinforcement on the local mechanical response. It has a rectangular shape and consists of the filler (circular GnP), the polymer and the interaction volume between them, as presented in figure 8. The thickness $T$ of the unit cell is estimated by equation (4), where $d$ is the filler diameter, $t_i$ is the filler thickness and $V_f$ is the filler volume fraction in the unit cell, while its width $W$ is given by equation (5). The interaction volume surrounding the particle has a thickness $t_{\text{int}}$. It is assumed that the particle has orthotropic elastic properties, while the interphase and epoxy are considered isotropic. The GnP has the same properties with single-layer graphene [26], which is another approximation. The material variables and parameters are summarised in table 1. The unit cell was parametrically analysed, accounting for unit cell volume fraction, interphase thickness $t_{\text{int}}$ and stiffness $E_{\text{int}}$, as presented in table 2.
These three phases are represented by 3D 8-node structural solid elements (SOLID185) using ANSYS 16.2, a commercially available finite element package. The finite element model is shown in figure 9, where the top view, 1/4 isometric view and through the thickness detail of the unit cell model are shown.

To calculate the elastic properties of the unit cell, it is subjected to the following loading conditions, as presented in figure 10. The elastic modulus in the x direction \( E_x \) is obtained by fixing the one side of the unit cell and pulling the opposite one in the x direction by a displacement of \( \Delta l \). The other two sides are constrained to have uniform displacement in the y-axis, while the top and bottom surfaces have uniform displacement in the z-axis (figure 10(a)). Similarly, the elastic modulus in z \( E_z \) is calculated. The bottom surface is fixed and the top one is pulled in the z direction by \( \Delta l \). The planes vertical to the x-axis have uniform displacement in the x direction, while the ones vertical to the y-axis have uniform y direction displacement (figure 10(b)). Finally, the shear modulus is found by fixing the one side and pulling the opposite one in the y direction for xy-plane shear modulus (figure 10(c)) and in the z direction for yz-plane modulus (figure 10(d)). The elastic properties are calculated based on Hooke’s Law and micromechanics.

### 3.2. Representative volume element

In the RVE, the nanocomposite architecture is taken into account. The elastic properties obtained in the unit cell are distributed in the RVE’s volume to simulate the filler dispersion, while the elements’ local coordinate systems are rotated to approach the filler orientation. The RVE is a cube with a side length of \( k \cdot d \), where \( d \) is the diameter of the GnP and \( k \) equals to 5. The value of \( k \) was initially derived by the works of [27, 28], while this RVE size has
been shown to successfully represent the graphene/polymer nanocomposite architecture in the research of [29] on the simulation of electrical conductivity and permittivity, and of [30] on the estimation of the thermal conductivity of graphene/polymer nanocomposites. The RVE is meshed with \( n \) elements (equation (6)). Therefore, each side is divided by \( n^{1/3} \). Based on the work conducted for the prediction of the electrical response [29] and thermal conductivity [30], which accounted for the different filler distribution on approaching nanocomposite architecture, Gaussian distribution has been chosen to approach the filler dispersion with the reinforcement volume fraction being the distribution mean value (\( \mu \)) and its standard deviation (\( \sigma \)) set as a parameter to be studied. The effective elastic modulus is modelled as before by fixing the one side and pulling the other in the opposite direction. Considering a GnP/epoxy nanocomposite loaded with 5.0 vol\% GnP, the effect of standard deviation was studied and presented in figure 11. It could be seen that by decreasing the standard deviation, the Young’s modulus decreases and it converges to a steady value for \( \sigma = \mu / 8 \). For the rest of the analysis, the standard deviation is set to \( \sigma = \mu / 8 \).

Figure 9. (a) Top view, (b) 1/4 isometric view and (c) through the thickness detail of the unit cell finite element model.

Figure 10. Unit cell loading conditions for obtaining the elastic tensile modulus in (a) xy plane and (b) through the thickness (z-axis) and the shear modulus in (c) xy plane and (d) yz (or xz) plane.
3.3. Modelling results

The simulation results of elastic modulus are summarised in figures 12 and 13 along with the experimental data presented in section 2.4. At first, it could be noted that the elastic modulus increases linearly with GnP loading. This linear trend was also observed in other numerical work [17]. Setting the interphase stiffness constant, the effect of interphase thickness is revealed in figure 12. Increasing the interphase thickness, the Young’s modulus increases accordingly. Considering that the properties of GnP and matrix varied distinctly, a larger interphase area helps to reduce the discontinuity and normalises the stress distribution between the two phases. The influence of interphase stiffness on Young’s modulus is shown in figure 13. The thickness of the interphase was fixed at 1.5 nm with the modulus varying from \( m = 0.25 \) (0.62 GPa) to \( m = 2 \) (4.94 GPa). The elastic modulus rises with increasing interphase stiffness, although its effect tends to be eliminated and values aggregate to the ones for interphase of 4.94 GPa (\( m = 2 \)). Load is transferred from epoxy to particle more efficiently for stiffer interphase, improving the overall nanocomposite performance. These results are found to be consistent with other researchers’ numerical studies [16, 19, 31], who either employed more complicated and demanding computational methods (atomistic structures, etc) or studied the interphase of different nanocomposites (i.e.

\[
\eta = \frac{4dk^3}{\pi T}. \tag{6}
\]
silica/epoxy), therefore extending these observations to graphene/polymer nanocomposites obtained by a more applicable finite element model.

Accounting for the experimental data, the simulation overestimates the elastic properties attributed to a number of factors. At first, the GnP particle has been assumed to exhibit the performance of single-layer graphene. However, it consists of several graphene layers with fabrication-induced imperfections, therefore reducing its mechanical properties. Moreover, the GnP dispersion does not consider the formulation of agglomerations, which act as stress concentration points and decrease the mechanical properties. Last but not least, both from simulation results and SEM images, a weak interfacial volume with small thickness is indicated. The interaction between the filler and epoxy is based on van der Waals forces, while the load transfer is achieved through friction instead of chemical bonding, and platelet functionalisation could improve performance. This finding is further supported by the experimental work of Poutrel et al [6], Pullicino et al [5], Wang et al [3] and King et al [4], where poor adhesion/interaction between the epoxy and non-functionalised GnP was observed on SEM images (clean smooth appearance of GnP, cracks along the interface, GnP pull-out) [3] and Fourier transform infra-red spectroscopy [5].

3.4. Stress–strain response simulation

Accounting for the observations made by the comparison between the experiment and the simulation, a new simulation attempt is made. The interfacial interaction is approached by contact elements. Contact elements (CONTA170) are surfed on the filler surface and target elements (TARGE170) are created on a polymer surface. Their interaction is defined by no separation contact behaviour and cohesive zone material behaviour for interfacial debonding. The cohesive zone model is bilinear with linear softening characterised by maximum traction and maximum separation. The normal contact stress and contact gap curve are presented in figure 14. In this debonding material behaviour, $P$ is the normal contact stress, $K_n$ is the normal contact stiffness, $u_n$ is the contact gap, $u_n^c$ is the contact gap at maximum normal contact stress (tension), $d_n$ is the debonding parameter and $\sigma_{\text{max}}$ is the maximum normal contact stress at tension. To estimate the maximum stress $\sigma_{\text{max}}$ at which debonding between particle/polymer occurs, we assume that there is a critical GnP/polymer nanocomposite structure that will fail only under the debonding of filler/matrix and its propagation from particle to particle until the final specimen failure. The matrix will not develop significant plastic strains and the filler breakage does not take place. In this case, the failure stress could be directly linked to debonding stress. This structure could be approached/compared to a nanocomposite structure on electrical percolation. The particles are positioned forming paths that could conduct/propagate electrons/debonding from the one end of the component to the other. For this structure, based on the work of [6, 28, 32], the percolation threshold of such a structure is estimated to be around 18%. Assuming that the trendline of the experimental tensile strength to nanocomposite volume fraction would be retained for greater volume fractions, the tensile strength of 18 vol% GnP/epoxy nanocomposite could be estimated around 22.35 MPa. Therefore, for this simulation, the $\sigma_{\text{max}}$ is set at 22.35 MPa and the $u_n^c$ is 100 nm, which is a sufficient contact gap relative to the size of the model to activate properly the debonding algorithm. Along with these parameters, artificial damping should be defined. Debonding is accompanied by convergence difficulties in the
Newton–Raphson solution. Artificial damping is used in the numerical solution to overcome these problems. The debonding parameter with viscous damping, \( d_v \), is calculated using the debonding parameter \( d \) and the incremental change in the debonding parameter \( \Delta d \) as equation (7), where \( \Delta t \) is the time increment, \( d_{old} \) is the debonding parameter at the previous sub-step, \( \Delta d \) is the increment in debonding parameter in the current sub-step and \( \eta \) is the damping coefficient. This viscous regularised debonding parameter \( d_v \) is used in the calculation of contact tractions when damping is activated. The damping coefficient has units of time and it should be smaller than the minimum time step size so that the maximum separation values are not exceeded in the debonding calculations [33]. In this case, the damping coefficient \( \eta \) is set to 0.40.

The epoxy behaviour is simulated by two methods. In the first one, a multi-linear elastic model is adopted to simulate the stress–strain behaviour (black solid line in figure 15(a)). In the second method, damage initiation and evolution model is assumed, while its stress–strain behaviour is linear (black solid line in figure 15(b)). For damage initiation, the failure stresses are summarised in table 3, while damage evolution is based on a maximum

![](image1)

**Figure 14.** Normal contact stress and contact gap curve for bilinear cohesive zone material [33].

![](image2)

**Figure 15.** Numerical stress–strain curves of GnP/epoxy nanocomposite for (a) multi-linear elastic matrix and (b) linear elastic matrix with damage initiation and evolution.

| Table 3. Epoxy stress for damage initiation. |
|---------------------------------------------|
| **Failure stress \( \sigma_{f} \)[MPa]**      |
| Tensile strength (x, y and z direction)      | 60.0 |
| Compressive strength (x, y and z direction)  | −60.0|
| Shear strength (xy, yz and xz plane)         | 42.4 |

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stress failure criterion. The tensile strength of epoxy was the minimum experimental value obtained during this work, the compressive strength of the epoxy was assumed to be equal and opposite to the tensile strength, while the shear strength was estimated to be the maximum shear stress when the material fails under uniaxial principal stress

\[
\tau_{\text{max}} = \sigma_T \frac{\sqrt{3}}{2} = 60 \frac{\sqrt{3}}{2} = 42.4 \text{ MPa}
\]

\[
d_e = d_{\text{old}} + \frac{\Delta t}{\Delta t + \eta} \Delta d.
\] (7)

The simulation results are presented in figure 15, where the polymer is approached by (a) a multi-linear elastic response (the material behaviour described by a piece-wise linear stress–strain curve, with successive slopes could be greater than the preceding slope, but no slope can be greater than the elastic modulus) and (b) linear elastic model with damage initiation and evolution for volume fraction \(V_f\) ranging from 2.5%–7.5%. In both cases, the elastic modulus increases with filler loading, while the tensile strength decreases, as was observed experimentally. Comparing the experimental curves with the numerical ones in figure 16, the effect of assumptions and simplifications made could be seen. Both polymer models correlate with each other and the measured data in the elastic range. Regarding the failure properties, the assumption of multi-linear elastic polymer behaviour overestimates the failure stress, while assuming linear response but accounting for damage initiation and propagation, the composite strength is underestimated. Therefore, it could be said that the two numerical approaches could define the upper and lower boundary values of the examined GnP/epoxy nanocomposites. The discrepancies found can be attributed to the polymer model assumption. As far as the multi-linear elastic polymer behaviour is concerned, the full stress–strain response of the polymer is accounted, but the epoxy failure mechanisms are not employed in the model. Therefore, the epoxy could develop stress/strains of its plastic region, but initiation and propagation of damage are not simulated. As a result, the matrix failure introduced by the interfacial fracture is not studied and evolved in the model. On the other hand, when linear elastic behaviour along with damage mechanisms are applied, the polymer strength is reached for lower strain compared to experimental value, and the nanocomposite failure would be achieved at lower values than those measured. Finally, this model is appropriate for estimating the elastic behaviour of the material, but for its complete stress–strain response, it is necessary to combine the matrix stress–strain behaviour with its fracture characteristics on a progressive damage model.

Figure 16. Comparison of experimental and numerical stress–strain curves for (a) 2.5 vol%, (b) 5.0 vol% and (c) 7.5 vol% GnP/epoxy nanocomposite.
4. Concluding remarks

The tensile and flexural stiffness and strength properties of a graphene nanoplatelet (GNP) reinforced polymer, Grade M25 GnP/Araldite LY564 under quasi-static conditions were measured. This was followed by a multiscale finite element model developed to describe the tensile behaviour of the nanocomposite. The model was employed for a specific type of structure and compared with its corresponding experimental results produced within the frame of this research study. Five sets of GnP/epoxy nanocomposite specimens with weight fraction ranging from 0–7.5 wt% were manufactured with the use of shear mixer. The material mechanical characterisation was conducted with tensile and bending tests, while SEM was applied for phase and failure mode identification. The elastic tensile and bending moduli were increased with particle loading, as expected, while the strength was decreased with filler concentration as a consequence of the weak interfacial interaction between the filler and the matrix, observed as debonding between particle/matrix on SEM images, as well as the increased formation of agglomerations with increased particle volume fraction. Accounting for the experimental observations of the finite element model, the elastic response was successfully approached, while the prediction of nanocomposite strength was bounded by two different assumptions in the analysis—multi-linear elastic polymer and linear elastic polymer with damage. The nanocomposite strength was shown to be lower than that of the neat epoxy, while it decreased with volume, as was found in experimental work. For more accurate strength predictions, it is suggested that a progressive damage approach be used where the combination of multi-linear elastic-plastic polymer behaviour accompanied by damage initiation and progression algorithms account for material softening in the presence of damage.

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