Finite Element Modelling of the Mechanical Behaviour of Graphene Nanocomposites

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Abstract

Graphene is a state-of-art material, known by its unique mechanical, thermal, optical and electrical properties. For this reason, the technical and scientific communities have been exploring its immensity of applications in the last few decades. Presently, the excellent mechanical behaviour of graphene has leading it to be employed in composite materials with notable capability of improvement. In this dissertation, a two-level finite element analysis is developed to address the behaviour of composite material reinforced with graphene. First, the mechanical properties of pristine graphene are extracted through a refined finite element model that simulates its nanostructure, and where covalent bonds are regarded as structural elements. Then, the atomistic representation of graphene is assembled into a suitable representative volume element to extract the elastic moduli of nanocomposite material. The final part of this document investigates the effects in the elastic behaviour of nanocomposite when atomic defects are introduced in graphene. The present approach is able to reproduce the elastic properties of pristine graphene in agreement with other methodologies, revealing also that orthotropic behaviour earlier predicted gives rise to isotropy for square sheets with larger dimensions. Additionally, the representative model of nanocomposite shows that increasing mechanical enhancement is achieved when higher adhesion is considered between graphene and surrounding matrix. Ultimately, it was identified that graphene with low defect content is capable to maintain its superior reinforcing effect in nanocomposites.

Keywords: Finite Elements, Graphene, Nanocomposite, Mechanical Properties, Atomic Defects

1. Introduction

Graphene is an atom-thick layer of carbon atoms in a repeating pattern of hexagons in honeycomb, as shown in figure 1. After its experimental discovery [1], the investigation on the mechanical properties of graphene has been a very active field of research in recent years. Having a Young’s modulus of almost 1 TPa and an intrinsic strength and strain near 130 GPa and 25%, respectively, graphene is the strongest material ever measured [2]. Another interesting find was that the mechanical response of graphene is strongly size-dependent, for small sizes up to 10 nm [3].

![Figure 1: Chirality of single-layered graphene.](image)

With such superior properties and a large specific area, graphene sheets are considered as ideal materials for composite reinforcement. Several experiments have been conducted, using reduced of functionalised graphene to increase surface chemical reactivity and achieve better dispersion within the matrix. However, crucial challenges arise from those experiments. Different morphologies of graphene are yielded from nanocomposite processing methods, depending on the its exfoliation level and dispersion quality, influencing the interfacial adhesion and surface contact between matrix and nanofiller [4,5]. Besides, the lack in improvement quality may be justified by natural imperfections and growth-induced defects, usually present in produced graphene. Those structural defects have been extensively studied in recent years, revealing their intrinsic relation with the deterioration of the overall mechanical performance of graphene [6–9]. As a result, the enhancement of various properties of the resulting composites may be severely reduced but not much attention has been given to explore this field.

In fact, the computational effort of more complex methods increases exponentially when one desires to research on the micro-cluster morphology and its properties – resulting from incorporating graphene
nanosheets in composite materials. As such, complex numerical approaches on this topic reported in the literature are scarce. However, the finite element analysis (FEA) has been applied when nanoscopic and microscopic formulation concepts should be included in a single computational model, due to its low computational cost and modelling capabilities [10,11].

In the present report, a multi-scale finite element (FE) model is developed to study the mechanical behaviour of a graphene-based nanocomposite. The first objective is to obtain a refined FE model capable of simulating the elastic behaviour of pristine graphene and validating it against other more rigorous methods available in the literature. Then, the surrounding matrix is modelled as a three-dimensional continuum medium and reinforced with the graphene sheet earlier obtained. To simulate the overall stress transfer, a homogeneous interface of specific thickness is also considered, which represents the percentage of surrounding matrix that is strongly affected by the presence of nanofiller. The second objective is to validate the nanocomposite FE model in comparison with other similar approaches and experimental results. Lastly, it is intended to incorporate atomic defects in graphene nanostructure and explore their effects on the effective mechanical properties of the nanocomposite. To the author’s best knowledge, the application of FEA for investigating the influence of defective graphene in nanocomposites, is here reported for the first time.

2. Computational Procedures

The present section describes the formulation and implementation of the FE models. ANSYS® Mechanical APDL 15.0 software was chosen to apply the technique.

2.1. Graphene Finite Element Model

The pristine graphene sheet was modelled at nanoscale implementing an equivalent space-frame representation of its molecular structure, based on energy correspondence between molecular mechanics and structural mechanics. For a nanostructured material, the covalent forces between individual atoms are described by the sum of the overall energetic contributions for each interaction, constituting a molecular force field (MFF). Due to the nature of this nanomaterial, the loading conditions were applied only parallel to its surface and considering only small deformations. Based on these arguments, it is valid to contemplate only the covalent energetic terms corresponding to bond stretching and bond-angle variation, and to neglect the much weaker non-covalent terms.

The next step is the definition of the geometrical properties of graphene nanostructure. Having as basis an unit hexagon of carbon atoms (Fig. 2), one assumed that nodal positions, element length L, and element cross-sectional diameter D, were defined accordingly. The default bond length was set to be $a_{cc} = 1.39 \text{ Å}$, which is within the range of bond length variation found in [12].

![Figure 2: Schematic of (a) an unit hexagon of carbon atoms and (b) geometrical properties of the carbon-carbon bond.](image)

Therefore, two distinct FEs were selected to simulate the covalent bond between carbon atoms, LINK180 and BEAM4. The first is an uniaxial and two-node tension-compression element with three translations at each node, while the second is an uniaxial two-node Euler-Bernoulli structural beam that has six degrees of freedom – three translations and three rotations – per node. Next, the forces equivalent to atomic bonds were obtained using the concept of equivalent bond material.

The first formulation is relative to LINK180 and resembles the one proposed in [15], where only bond stretching ($k^s$) and bond-angle variation ($k^b$) interactions are needed to simulate the equivalent carbon-carbon bond. The equivalent Young’s moduli for bond stretching and bond-angle variation terms were obtained as explained in the aforementioned report. The formulation for BEAM4 is based on the one proposed in [16], but neglecting Timoshenko shear deformation in accordance to element theory. The versatility of this element allows to use only a single beam for each carbon-carbon bond, having equivalent Young’s modulus and shear modulus as defined in [16]. Moreover, it was assumed an equivalent isotropic material for the equivalent beam, and the condition for its Poisson ratio $\nu = -1 + E/2G$ with $-1 < \nu < 0.5$ took to the following maximum condition:

$$D < \sqrt{1 + \nu} \sqrt{\frac{16k^s}{k^d}}$$  \hspace{1cm} (1)$$

where bond torsion term $k^t$ was incorporated and the beam diameter $D$ was determined using the maximum value obtained with Eq. (1). The parameters of
Table 1: MFF constants used in pristine graphene FE model.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LINK180 BEAM4</td>
<td>LINK180 BEAM4</td>
<td></td>
</tr>
<tr>
<td>$k^a$</td>
<td>32.6</td>
<td>42.3</td>
</tr>
<tr>
<td>$k^b$</td>
<td>4.38</td>
<td>4.5</td>
</tr>
<tr>
<td>$k^s$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>2.78</td>
<td>2.78</td>
</tr>
</tbody>
</table>

2.2. Nanocomposite Finite Element Model

The polymeric nanocomposite (denoted as C) was analysed as a triple-layered representative volume element (RVE), called sandwich-like model (Fig. 4). The single-layer of graphene (denoted as G) was positioned at plane $z = 0$, while being covered on both sides by matrix (denoted as M) volumes with the same finite thickness value. To represent the matrix behaviour, a continuum isotropic modelling was preferred from a molecular one in order to avoid higher computational cost and complexity, as done in other works [10, 11]. As such, a three-dimensional hexahedral FE was used for the volume discretization, SOLID185. This isotropic element has eight nodes and three translations per node. The values of Young’s modulus and Poisson’s ratio were taken equal to those of common epoxy resin, $E_M = 3$ GPa and $\nu_M = 0.34$, respectively.

In between these two basic phases, a continuum isotropic interface volume (denoted as I) was modelled separately of the bulk matrix, with hexahedral FEs as well. The interfacial region is a significant part of any composite, as it is responsible for the overall interfacial load transfer. In this approach, the filler phase was assumed exfoliated and uniformly dispersed. As such, the interfacial contact between graphene and epoxy is the largest possible and its stiffness is related to the level of interfacial adhesion. Therefore, the modelling of complex phenomena was avoided but the effects of higher density distribution of polymeric chains due to the presence of the reinforcement, found in [5], can be efficiently accounted.

For convenience, the transversal dimensions of the matrix volume were the same as those of graphene ($L_x$ and $L_y$). The RVE total volume $V_C$ is dependent on the reinforcement volume fraction $V_f$ as it follows:

$$V_f = \frac{V_G}{V_C}$$

(2)

where $V_G$ is the volume of graphene filler. Seeing that transversal size is uniform along RVE thickness (along Z-axis), it follows that Eq. (2) can be rewritten as:

$$V_f = \frac{t^G}{t^C}$$

(3)

where $t^G$ and $t^C$ are the thicknesses of graphene and RVE, respectively.

Despite that graphene has no real thickness, from a physical point of view, this value may be defined as the normal distance – from the atomistic structure of graphene – wherein interfacial interactions occur. Since in the present RVE, epoxy was covering graphene on both sides, it was assumed that thicknesses for interface ($t^I$) and graphene are the same. Thus, the total interface region takes place from $z = 0^+$ to $z = +t^I$ and from $z = -t^I$ to $z = 0$ (see Fig. 4).

On the one hand, the graphitic inter-planar distance of 3.4 Å is commonly used as interface thickness, though that methodology does not take into account the type of matrix and its respective equilibrium distance with graphene surface. Accordingly, an interface thickness equal to the equilibrium distance $r_{\text{min}} = 3.8163$ Å of van der Waals (vdW) interactions
between a carbon atom and a polymer chain \( CH_2 \) was preferred. This value was obtained using the 12-6 potential of Lennard-Jones with parameters taken from [17], as done in [18]. The curves obtained for interatomic potential and its derivative, interatomic force \( F(r) \), are similar to those exemplified in Fig. 5.

Such non-covalent force along the interface enabled the implementing of a structural finite element to represent it. The choice was to use COMBIN39, an uniaxial spring element defined by two nodes, each with three translations, and a non-linear force-deflection capability. For simplicity reasons, only vdW interactions from a carbon atom facing directly a nodal position of the inside surface of matrix were considered.

The final step is to perform the RVE volume meshing. Since graphene sheet and interface are connected at plane \( z = 0 \), line elements (BEAM4) and solid elements (SOLID185) must have coincident nodal positions, compliant with graphene nanostructure. Therefore, regular rectangular discretization was used to accomplish a suitable coupling, as depicted in Fig. 3(a). This operation may be applied since both element types are three dimensional while having common degrees of freedom per node. In respect to other interactions, appropriate nodal coupling took place between elements COMBIN39–BEAM4 at plane \( z = 0 \), as well between elements SOLID185–COMBIN39–SOLID185 at plane \( z = +t_I \). In its turn, discretization along RVE thickness is dependent on its total volume, which depends also on volume fraction of reinforcement. For the homogeneous interface, from \( z = 0^+ \) to \( z = +t_I \), it was decided to use uniform divisions, whereas an expansive growth division was applied for the matrix, from \( z = +t_I \) to \( z = +t_C \) as shown in Fig. 3(c). The other half of the RVE was meshed symmetrically. An example of volume mesh obtained for the RVE is presented in Fig. 3(b).

2.3. Incorporation of Atomic Defects in Graphene

The most common structural defect that is referred in literature is the vacancy-type. To investigate the influence of these atomic defects, in a group of samples of FE model of the nanocomposite, the reinforcement of graphene sheet was degraded by inserting single-vacancy (SV) type defects randomly located.
Considering the total surface area of a single pristine sheet, these defects were generated only inside an area fraction, where it is expected the stress and strain distributions are not influenced by boundary conditions.

As SV defect type is introduced when a carbon atom is removed from the graphene lattice, the three covalent bonds which connect the removed atom to its neighbours must be also neglected. In terms of modelling, the process of defect introduction was performed by removing the respective node, coincident with the atom to be withdrawn, and the structural elements that are linked to it (see Fig 6). One may repeat the latter process as many times as the total number of defects desired, though nonphysical defect coalescence, when highly defective condition is considered. Moreover, to avoid the formation of a double-vacancy (DV) complex, the relative distance between two neighbour vacancies must be larger than 4 Å [7]. To avoid these events, the latter value was assumed as minimum distance between neighbour SVs.

Figure 6: Introduction of a SV defect (red dot) in graphene nanostructure.

As referred earlier, it was decided to simulate the randomness of defect distribution rather than a set of predefined locations, as conducted by several other authors [6,7,9]. A suitable quantification of the defective condition of graphene is the defect concentration percentage DC (%), defined as:

\[
DC(\%) = \frac{\text{No. of Removed Atoms}}{\text{Total No. of Atoms}} \quad (4)
\]

3. Numerical Results and Discussion

The present section exhibits the results computed with the multi-scale FE model described in Section 2. Subsequently, their discussion and validation is conducted by comparing with similar results found in literature.

3.1. Elastic Properties of Pristine Graphene

First, the global coordinate system (X,Y,Z) has its X-axis aligned with the zigzag direction while the Y-axis is aligned with the armchair direction. The Z-axis is not yet used in this first model, as graphene is a two-dimensional material. In terms of dimensions, two square shape sheets were constructed with approximately 24 Å and 70 Å per side, respectively, as shown in Fig. 7.

![Figure 7: Square graphene sheets built with (a) 24 Å and (b) 70 Å per side, respectively - images from ANSYS®.](image)

At this stage, specific boundary conditions and displacement conditions were applied into the pristine sheet. These conditions are related to the elastic properties of graphene which this report aims to determine – \(E_x, \nu_{yx}, E_y, \nu_{xy}, G_{xy}, K_{xy}\) –, obtained through the following mechanical tests:

- **Uniaxial tensile test in the zigzag direction**

  \[
  E_x = \frac{(\sum R_x)/L_y}{\sum l_x/L_x} \quad \nu_{yx} = -\frac{2(\sum \triangle l_y')/L_x}{\sum \triangle l_x}/L_y \quad (5)
  \]

- **Uniaxial tensile test in the armchair direction**

  \[
  E_y = \frac{(\sum R_y)/L_x}{\sum l_y/L_y} \quad \nu_{xy} = -\frac{2(\sum \triangle l_x')/L_y}{\sum \triangle l_y}/L_y \quad (6)
  \]

where \(\sum R_x\) and \(\sum R_y\) are the sums of nodal reaction forces in the fixed edges, \(\sum l_x\) and \(\sum l_y\) are the deformations applied for an axial strain of 0.01% and \(\sum \triangle l_x'\) and \(\sum \triangle l_y'\) are the averaged sums of nodal displacements in transverse directions.

- **Pure shear test**

  \[
  G_{xy} = \frac{\left(\frac{\sum F_x}{L_x} + \frac{\sum F_y}{L_y}\right)}{\gamma} \quad (7)
  \]

- **Biaxial tensile test**

  \[
  K_{xy} = \frac{\left(\frac{\sum F_x}{L_x} + \frac{\sum F_y}{L_y}\right)}{\Delta} \quad (8)
  \]

where \(\sum F_x\) and \(\sum F_y\) are the sum of nodal forces on the edges due to the imposed transverse displacements relative to shear strain \(\gamma\) and bi-axial displacements relative to area expansion \(\Delta\).

All mechanical tests were performed assuming static linear simulations on ANSYS®. Applying the expressions (Eqs. (5)-(8)) abovementioned, the set of elastic properties computed for graphene is exhibited.
Table 2: Elastic properties predicted for graphene using the present approach and other works available in literature.

<table>
<thead>
<tr>
<th>Size Sheet</th>
<th>FE Type</th>
<th>MFF</th>
<th>$E_x$ (nN/nm)</th>
<th>$E_y$ (nN/nm)</th>
<th>$\nu_{xy}$</th>
<th>$G_{xy}$ (nN/nm)</th>
<th>$K_{xy}$ (nN/nm)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 Å</td>
<td>LINK180</td>
<td>AMBER</td>
<td>231.7</td>
<td>216.7</td>
<td>0.443</td>
<td>0.405</td>
<td>71.3</td>
<td>195.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Morse</td>
<td>243.2</td>
<td>228.3</td>
<td>0.468</td>
<td>0.426</td>
<td>73.5</td>
<td>214.5</td>
</tr>
<tr>
<td></td>
<td>BEAM4</td>
<td>AMBER</td>
<td>263.7</td>
<td>242.7</td>
<td>0.396</td>
<td>0.360</td>
<td>82.3</td>
<td>204.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Morse</td>
<td>296.7</td>
<td>274.4</td>
<td>0.476</td>
<td>0.432</td>
<td>87.3</td>
<td>264.7</td>
</tr>
<tr>
<td>70 Å</td>
<td>LINK180</td>
<td>AMBER</td>
<td>209.2</td>
<td>204.5</td>
<td>0.454</td>
<td>0.439</td>
<td>69.1</td>
<td>187.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Morse</td>
<td>219.1</td>
<td>214.4</td>
<td>0.479</td>
<td>0.463</td>
<td>71.1</td>
<td>205.2</td>
</tr>
<tr>
<td></td>
<td>BEAM4</td>
<td>AMBER</td>
<td>235.7</td>
<td>228.9</td>
<td>0.406</td>
<td>0.392</td>
<td>79.9</td>
<td>193.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Morse</td>
<td>263.5</td>
<td>256.0</td>
<td>0.489</td>
<td>0.471</td>
<td>84.2</td>
<td>250.9</td>
</tr>
</tbody>
</table>

Lee et al. [2] 335 – – Experimental
Reddy et al. [12] 277.4 228.1 0.520 0.428 60.9 – MM
Sakhaee-Pour [19] 354.3 353.6 – 75.0* – FEA
Scarpa et al. [16] 517.0 342 0.523 0.509 76.0 –
Kudin et al. [20] 345 0.149 – – Ab-initio
H. Zhao et al. [3] 343.1 0.210 – – MD
J. Zhao et al. [21] 291.2 327.8 0.143 0.157 84.6* –
Tsai and Tu [4] 310.1 0.261 121.7 –
Kalosakas et al. [22] 320 0.22 84.0 200.0

Superscript * – Mean of results for simple shear tests along each chiral direction.

In Table 2. Since graphene has no real thickness, the elastic moduli determined were defined in terms of nN/nm - denominated as surface elastic moduli.

Looking into literature, satisfactory resemblance in predictions on Young’s modulus is found on works from molecular mechanics (MM) [12], but also on ab-initio [20] and MD [4,21] simulations, when comparing with present results obtained from BEAM4 rather than from LINK180. Moreover, from a global perspective, it can be seen that Morse force field follows more accordingly the results relatively to Young’s modulus. However, it is observed a weak agreement with other works based in FEA [16,19], mainly due to differences in FE modelling. Moreover, both formulations presented are in conformity with the higher Poisson’s ratios reported elsewhere [12,16,19]. Regarding shear modulus, the present results are adjusted with the whole set of values found in literature. Spite of bulk modulus is not usually reported by researchers, the present approach is capable of predict consistent values with the outcome achieved from MD [22].

From Table 2, another remark concerns the differentiation in present results because of the choice of FE type and MFF. As both formulations depicted the nanostructure of graphene assuming different equivalent space-frames, the association of structural strain energies with MFF constants were distinct, as the characterization of equivalent bond too. Besides, for the same FE type, AMBER and Morse force fields provided diverse values of MFF constants (see Table 1). The contributions from each covalent interaction and their atomistic interrelation are specific and as such, their effects in graphene elastic properties. Despite of increasing Young’s modulus in respect to AMBER, Morse is also responsible for enlarging Poisson’s ratio, according to Table 2. This special behaviour of graphene is evidenced when comparing the effects of chirality in elastic properties as well. Although considering a square shaped sheet, the values of Young’s moduli and Poisson’s ratios are different along zigzag and armchair directions, for all the models analysed. Thus, both formulations are able to represent the orthotropic behaviour of graphene, as found in most of works in literature [12,16,19,21].

On the other hand, the construction of two sheets with different sizes was important to demonstrate the effects of size-dependent properties on graphene. As depicted in Table 2, the elastic properties are distinct between both sizes, but since the results along both directions are approximating mutually with the increasing size, the chirality influence gets minor too. A similar achievement is reported in [3]. Therefore, it was considered more suitable to use as reinforcement a pristine sheet whose mechanical performance is size independent. Thus, the study on convergence of elastic properties of pristine graphene with increasing diagonal length $L$ was performed, using the modelling case implemented with BEAM4 and Morse as MFF. The results are shown in Fig. 8, for an interval of diagonal lengths between [34 ; 258] Å. The set of sheet dimensions, number of nodes and elements may be consulted in Table 3.

As one may verify in Fig. 8, the results obtained corroborate the hypothesis of isotropic behaviour of graphene and also show the elastic properties converging to bulk values. To minimize the computational cost and guarantee enough size-independent
behaviour, the graphene model constructed with a diagonal length around 150 Å (sheet 4 in Table 3) was used as reinforcement in the RVE of nanocomposite.

Table 3: Geometry and discretization of graphene FE models used to obtain bulk values for elastic properties.

<table>
<thead>
<tr>
<th>Sheet</th>
<th>$L_x$ (Å)</th>
<th>$L_y$ (Å)</th>
<th>$L$ (Å)</th>
<th>Nodes</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.1</td>
<td>23.6</td>
<td>33.7</td>
<td>252</td>
<td>356</td>
</tr>
<tr>
<td>2</td>
<td>40.9</td>
<td>40.3</td>
<td>57.4</td>
<td>700</td>
<td>1013</td>
</tr>
<tr>
<td>3</td>
<td>69.8</td>
<td>69.5</td>
<td>98.5</td>
<td>2006</td>
<td>2946</td>
</tr>
<tr>
<td>4</td>
<td>103.5</td>
<td>102.9</td>
<td>145.9</td>
<td>4350</td>
<td>6432</td>
</tr>
<tr>
<td>5</td>
<td>139.6</td>
<td>140.4</td>
<td>198.0</td>
<td>7956</td>
<td>11808</td>
</tr>
<tr>
<td>6</td>
<td>183.0</td>
<td>182.1</td>
<td>258.1</td>
<td>13 464</td>
<td>20032</td>
</tr>
</tbody>
</table>

3.2. Elastic Behaviour of Graphene Nanocomposite

The elastic behaviour of the nanocomposite was investigated for several values of volume fraction and interface stiffness. For these parametric studies, different volume mesh discretizations were used accordingly to each volume fraction (see Table 4). To compute the elastic properties of the RVE, the Eqs. (5)-(8) were applied considering all stresses in units of force per area, by dividing the respective surface stress by the total thickness $t^C$ of the model. After proper mesh convergence, the final results obtained were determined using the method of Newton-Raphson on ANSYS©.

As first approximation, the proposed RVE was assumed to have no interface, i.e. $E_I = E_M$, whose results obtained are shown in Fig. 9. The results concerning this case study may be compared with the rule of mixtures (ROM) concerning uniform deformation, and expressed as:

$$p_{ij}^C = p_{ij}^G V_f + p_{ij}^M (1 - V_f)$$  \hspace{1cm} (9)

where $p_{ij}^G$ and $p_{ij}^M$ are the mechanical properties of reinforcement and matrix, respectively, while $p_{ij}^C$ is the one predicted for the resulting RVE of nanocomposite.

To validate the FE model of graphene-based nanocomposite, the results of the parametric study concerning the effects of volume fraction are confronted with other similar approaches reported in literature, as depicted in Fig. 9. First, one may verify that present results are almost exact with the theoretical approach based in ROM. This was expected since both approaches have concordant assumptions, but it would not have been possible to solve the problem here defined with the limitations from ROM, since the latter does not account for atomistic effects. Besides, works from other authors [10, 11] also reveal linear enhancement in elastic properties of the nanocomposite with progressive increments of volume fraction. When no interface is considered, the numerical prediction from [10] is concordant with the proposed RVE. The small discrepancy between both is due to the FE model of graphene implemented as reinforcement, thus occurring dissimilar enhancement. However, the discrepancy aggravates when a hybrid interface is assumed.

For the parametric study concerning the influence of interface stiffness, other cases where $E_I = 2 \times E_M$ and $E_I = 4 \times E_M$ are shown in the following Fig. 10. While the present approach admitted an interfacial region with uniform mechanical behaviour but low adhesion modulus, works from [10, 11] adopted a hybrid interface with mechanical properties bounded by the respective ones of the two materials that surround it, providing the means for a reinforcing effect much superior than those obtained in cases with $E_I = 2 \times E_M$ and $E_I = 4 \times E_M$. Although the use of

Figure 8: Evolution of elastic properties of pristine graphene in respect to the lattice diagonal length $L$.
Table 4: Volume mesh discretization used in the RVE of nanocomposite for different volume fractions.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_f )</td>
<td>No. of solid elements</td>
</tr>
<tr>
<td>0.02</td>
<td>50,912</td>
</tr>
<tr>
<td>0.04</td>
<td>50,912</td>
</tr>
<tr>
<td>0.06</td>
<td>50,912</td>
</tr>
<tr>
<td>0.08</td>
<td>50,912</td>
</tr>
<tr>
<td>0.10</td>
<td>50,912</td>
</tr>
</tbody>
</table>

Figure 9: Comparison on normalized Young’s modulus in zigzag direction \( E_x/E_M \) versus volume fraction \( V_f \).

homogeneous properties for interface is more simplistic, from a physical point of view, the polymer high density distribution that occurs near to graphene surface [5], may be represented by a volume of material with small thickness that allows to adjust the desired level of adhesion by changing its stiffness. Nevertheless, for higher volume fractions, when the distance between two successive filler particles is smaller or a larger sheet is embedded, it is expectable that a larger portion of matrix is transformed, with an interface thickness increasing considerably.

Table 5: Predictions on stiffness enhancement for graphene-epoxy nanocomposites.

<table>
<thead>
<tr>
<th>wt ( (%) )</th>
<th>Stiff. Enhanc. ( (%) )</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present</td>
<td>0.10</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.9</td>
</tr>
<tr>
<td>Numerical</td>
<td>[10]</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>[11]</td>
<td>0.10</td>
</tr>
<tr>
<td>Experimental</td>
<td>[23]</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>[24]</td>
<td>0.10</td>
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<td>14.4</td>
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Considering the stiffness enhancement provided by experiments reported in literature (see Table 5), which are usually expressed in weight percentage (denoted as \( wt \)), it can be verified a good correlation from the proposed RVE with experimental nanocomposites which have lower interfacial adhesion, as those reported in [23, 24]. On the other hand, the employment of hybrid interface leads to results more concordant with experiments where functionalisation of graphene is introduced, which provides a better load transfer and increasing reinforcing effect.

3.3. Influence of Defective Graphene in Nanocomposites

To study the effects of atomic defects, the FE model of defective graphene (DG) was substituted over that of pristine graphene (PG). The remaining geometry, material properties and spatial modelling for the FE model of nanocomposite were maintained. Next, using Eq. (4), five distinct values of \( DC \) were investigated - SV (0.023% \( DC \)) and multiple SV (0.25% \( DC \), 0.5% \( DC \), 1% \( DC \) and 2% \( DC \)) defects - and each concerning to a group of five different DG samples, which have defects randomly located. Hereafter, the mean values for the elastic properties were obtained from each group in the respective conditions of volume fraction and properly normalized using the respective value determined in the FE model of nanocomposite with PG. Additionally, the standard deviation on each property was computed to explore the randomness effect. The outcome is shown in Fig. 11.

By observing Fig. 11(a)-11(c), it is easily verified that the mechanical properties of graphene-based nanocomposite are indeed affected by atomic defects.
For the same volume fraction, the present results show a progressive deterioration of effective moduli while the concentration of multiple SV defects increases. In fact, the smallest influence in effective properties happens when an unique SV (0.023% DC) in introduced, while the largest reduction occurs for 2% DC. Moreover, it seems that bulk modulus is greatly influenced by the defective condition of reinforcement, when compared to the other two moduli.

Another interesting finding from Fig. 11(a)-11(c) is the repercussion of volume fraction in the mechanical performance of the nanocomposite reinforced with DG. The degradation of mechanical performance seems to have greater sensitivity to increasing volume fraction between 2% $V_f$ and 4% $V_f$ rather than increasing volume fraction from 6% $V_f$ to 10% $V_f$.

Concerning the impact of randomness in the results obtained, as shown in Fig. 11(d)-11(f), it becomes clear that this effect does not own a critical preponderance in the dispersion of the elastic properties, at least quantitatively (since the largest standard deviation is less than 1 GPa for all cases). Still, it becomes clear that for the same defect concentration, the absolute deviations tend to increase for greater volume fractions. On the other hand, while the defect coverage enlarges over the DG surface, for the same volume fraction, the sample standard deviation tends to increase but non-monotonically. This evidence can be a result of mutual interaction between stress fields generated by each isolated defect, as their random distribution may affect each elastic property in distinct ways.

4. Conclusions

The multi-scale computational model based on FEA, developed to describe the mechanical behaviour of a graphene nanocomposite, was accomplished. The latter method provided an useful comparison between numerical and experimental results and enabled one to bypass complex calculations to obtain first approximations to the problem defined. Despite of several limitations that do not allow to access other structure-property relations, the proposed RVE had the efficiency and practicability required to evaluate the mechanical behaviour of graphene-based nanocomposites with fairly accurate results. Moreover, several parametric studies were performed to explore the influence of atomic defects at nanoscale in the mechanical performance of the nanocomposite. Eventually, this section presents the conclusions and main discoveries found, as it follows.

First, the study of size effects confirmed that elastic properties of PG converge to bulk values, for a diagonal length of square-shape sheets above 10 Å, also proving that a large sheet of PG behaves almost as an isotropic material rather than orthotropic. In respect to graphene-based nanocomposite, the design of higher interface stiffness took to increasing adhesion between graphene and epoxy due to a more effective stress transfer between both materials. On the other hand, the effective elastic properties of the nanocomposite are not influenced by a fewer number of SV type defects, which shows that graphene is capable to maintain its superior reinforcing effect. However, the degrading effect on those properties increases upon the defective condition. Still, the influence of randomness of location/distribution of defects has not
resulted in an appreciable dispersion of effective elastic properties.

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References